

# SOIL SCIENCE

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## SOIL SCIENCE



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## THE INFLUENCE OF MANURE AND IRRIGATION WATER ON THE CARBON, PHOSPHORUS, CALCIUM AND MAGNESIUM OF THE SOIL

C. T. HIRST AND J. E. GREAVES

*Utah Agricultural Experiment Station*

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A low organic carbon content is a characteristic of the arid soils. This is due primarily to two causes: (a) a scant vegetation resulting from the meager rainfall which they receive and (b) their loose, well aerated structure that has given rise to a rich microflora, which in turn energetically decomposes plant residues. Ages have contributed to their present nitrogen and carbon content. Hence, there must have been reached within them an equilibrium which is governed by the climatic conditions, the physical, chemical, and biological properties of the soil. When these soils are brought under cultivation, conditions are changed; hence, we may expect a shifting of the equilibria which is sure to modify the organic material and soluble constituents within the soil. The small amount of work which has been done indicates that cultivation affects in a dissimilar manner the arid and humid soils (14, 16, 17) and increases the activity of their microflora (3). It has further been found that arid soils retain the nitrogen of organic manures to a greater degree than do the humid, and that their nitrogen content may be increased without decreasing their azofying powers or disturbing the relative proportion of nitrogen in the various foot sections (10).

Inasmuch as the nitrogen content of the humus of arid soil is high (14) as compared to humid soil, we are prone to ask: "Will this condition be maintained when the nitrogen content of the arid soil is increased by organic manures?" If this is the case there must result an even greater increase in bacterial activities (4). This results in the formation of larger quantities of organic and inorganic acids which react with the insoluble constituents of the soil, rendering them soluble. Such conditions extending over periods of years are certain to modify soils chemically, physically, and biologically. Therefore, the aim of this work is to determine the influence of manure and irrigation water on the organic carbon, carbon-nitrogen ratio, phosphorus, calcium, magnesium, and calcium-magnesium ratio of a typical highly calcareous loam soil.

### PLAN OF EXPERIMENT

The soil used in this work was obtained from the Greenville (Logan, Utah) experiment farm. The plats are 7 feet wide and 24 feet long with a 4-foot walk

dividing them. Each fall the land was plowed and left over until spring, when a mixture of fairly well-rotted manure was applied to the variously manured plats. The manure contained in each ton approximately 738 pounds of dry matter, 3.04 pounds of phosphorus, 13.7 pounds of potassium, and 16.08 pounds of nitrogen. The manure was thoroughly disked or plowed into the soil. Measured quantities of water were applied to the plats from flumes, as described in Utah Experiment Station Bulletins 115 to 120. They were kept free from weeds throughout the year. The quantities of water and manure applied to the various plats were as follows:

- 4 plats received no water and no manure
- 3 plats received 40 inches of water and no manure<sup>1</sup>
- 2 plats received 20 inches of water and no manure<sup>2</sup>

All of the above were repeated with plats receiving 5 and 15 tons of manure. Hence, the series included soil without manure, with 5 tons to the acre, and with 15 tons to the acre. The irrigation water applied varied from none to 40 inches both with and without manure. In addition to this, they received the average annual precipitation of approximately 18 inches. This of course, was uniform for all plats. The plats have received this treatment since the spring of 1911. In the fall of 1922 and again in the fall of 1923 composite samples for this work were carefully taken in foot-sections to a depth of 3 feet.

The soil is highly calcareous, of sedimentary origin, very uniform in physical composition even to a depth of 10 feet, rich in phosphorus, potassium and the other essential elements, with the exception of nitrogen which is low. The large quantity of calcium and magnesium which it contains is in the form of the double salt, calcium-magnesium-carbonate. It has a very active microflora (4, 10), and when supplied with optimum moisture and organic manure produces good crops (2).

The analyses were made according to the methods of the Association of Official Agricultural Chemists (1), the organic carbon by the dry-combustion method, the phosphorus by the sodium-peroxide method, the nitrogen by the method modified to include nitrates, and the calcium and magnesium by the standard digestion method.

The average, stated as pounds per acre of carbon found in the soil receiving the various treatments, is given in table 1.

The per cent of organic material of the first, second, and third foot of the unmanured soil is 1.60, 1.33, and 0.74 ( $c \times 1.724$ ), respectively. The soil which has received 5 tons per acre annually for the past 12 years contains 1.91, 1.17, and 0.79 per cent of carbon in the first, second, and third feet, respectively. The soil which had received 15 tons of manure yearly contained 2.59, 1.97, and 1.6 per cent of carbon in the various foot-sections.

<sup>1</sup> Water applied in 4 equal applications

<sup>2</sup> Water applied in 8 equal applications

Using Wolff's factor,  $c \times 1.724$ , for converting the carbon into organic material we find that the soil which had received yearly 5 tons of manure per acre had gained 7448 pounds of organic matter, which is 17.7 per cent of the organic material applied to these plats during the past 12 years. Hence, in addition to the native organic carbon, which in these plats we have no method of estimating, the bacteria have decomposed annually 2879 pounds of organic material. This is very close to the 3000 pounds which is often stated as being approximately the annual loss from a good arable soil. The soil which had received annually 15 tons of manure had gained 90,062 pounds of organic matter, which is 71.4 per cent of the applied manure. Hence, the heavily manured plats were decomposing the applied organic material at the rate of 3000 pounds per acre yearly, which is only 121 pounds more than was being decomposed in the lightly manured soil. Two conclusions can be drawn from these results: (a) The organic carbon content of this arid soil can be very materially increased by the application of organic manures; and (b) the yearly loss is not

TABLE 1

*Carbon found in the different foot-sections of soil receiving varying quantities of water and manure*

TREATMENT	POUNDS PER ACRE-FOOT (3,600,000) OF CARBON			
	First foot	Second foot	Third foot	Total
No manure.....	33,480	27,720	15,480	76,680
5 tons manure.....	39,960	24,480	16,560	81,000
15 tons manure.....	54,000	41,040	33,480	129,020
No irrigation water.....	44,640	29,880	23,040	97,560
20 inches irrigation water.....	42,480	33,840	22,680	99,000
40 inches irrigation water.....	39,960	29,160	19,800	88,920

much greater from heavy applications than from light, the decomposition being approximately 3000 pounds annually over that in unmanured soil.

With the exception of two irregular results appearing in the second foot, the quantity of organic matter in the soil decreased as the quantity of irrigation water applied increased. Hence, we find that the decomposition of organic matter in a soil increases as the irrigation water applied increases up to 40 acre-inches yearly. This is what is to be expected when we recall that bacterial activity is a function of the water content of the soil (5), and it has been shown that irrigation water was increasing the number and efficiency of bacteria in this specific soil (4).

The percentage distribution of the total carbon in the various foot-sections is shown in table 2.

There is not the uniformity in the distribution of the carbon in the various foot-sections which was found in the case of the nitrogen (5), yet it is evident that the organic carbon is quite rapidly carried to the second and even the third foot. This naturally raises the question as to how much of the carbon which has disappeared from the surface 3 feet of this soil has been carried be-

low the third foot-section. Probably considerable, especially where the larger quantities of water are being applied to the soil. The average percentage of the total organic carbon found in the first, second, and third foot-sections is 44.7 per cent, 32.6 per cent, and 22.6 per cent, respectively. The corresponding percentages of nitrogen in this same soil and in the corresponding foot-sections were found to be 41 per cent for the first foot, 33 per cent for the second foot, and 26 per cent for the third foot, thus showing that the nitrogen is carried downward more rapidly than is the organic carbon (10).

Where 5 tons per acre yearly had been applied, the soil had gained 1370 pounds of total nitrogen, or 486 pounds more than had been applied in the

TABLE 2  
*Total carbon found in soil receiving varying quantities of manure and irrigation water*

TREATMENT	FIRST FOOT	SECOND FOOT	THIRD FOOT
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
No manure.....	43.7	36.2	20.2
5 tons manure.....	49.3	30.2	20.4
15 tons manure.....	41.9	31.8	26.0
No irrigation water.....	45.7	30.6	23.6
20 inches irrigation water.....	42.9	34.2	22.9
40 inches irrigation water.....	44.9	32.7	22.3

TABLE 3  
*Carbon-nitrogen ratio in soil receiving varying quantities of manure and irrigation water*

TREATMENT	NITROGEN: CARBON IN VARIOUS FOOT-SECTIONS		
	First foot	Second foot	Third foot
No manure.....	8.9	8.6	7.0
5 tons manure.....	9.3	7.1	5.9
15 tons manure.....	11.5	11.3	10.7
No irrigation water.....	10.3	8.8	7.5
20 inches irrigation water.....	9.6	9.8	6.1
40 inches irrigation water.....	9.8	8.7	7.9

manure. The soil receiving 15 tons of manure to the acre yearly had gained 2248 pounds of total nitrogen. This is 405 pounds less than was actually applied to the soil. This retention of nitrogen over that of carbon has narrowed the carbon-nitrogen ratio over that found in the manure but has widened it within the soil.

With the exception of the second and third foot-sections in the plats receiving 5 tons per acre of manure yearly, the application of manure has widened the carbon-nitrogen ratio. In these two exceptions it cannot be due to experimental error, for these plats were carefully resampled and reanalyzed 12 months after the first sampling described in this work with the same results. The results therefore must be due to abnormal conditions within these two specific



plats, and it will be interesting and valuable to compare them with similarly obtained results in some ten years from now.

The tendency of irrigation water is to narrow the carbon-nitrogen ratio, which should be expected when one recalls that bacterial activities are dependent upon an optimum moisture content.

The somewhat narrow carbon-nitrogen ratio in the arid soils is due primarily to two factors: (a) The limited quantity of water in the soil tends to accelerate cellulose decomposition to a greater extent than it does the decomposition of protein; (b) the plant residues which reach the arid soil are relatively richer in nitrogen than are similar residues which reach humid soil. Hence, other things being equal, the richer plant residues would give a narrower carbon-nitrogen ratio (15).

The total phosphorus found in this soil is given in table 4.

TABLE 4

*Total soluble phosphorus found in the surface three feet of soil receiving varying quantities of irrigation water and manure*

TREATMENT	POUNDS PER ACRE OF PHOSPHORUS			
	First foot	Second foot	Third foot	Total
No manure.....	3,312	3,240	2,880	9,432
5 tons manure.....	3,492	3,312	2,988	9,792
15 tons manure.....	3,672	3,384	2,988	10,064
No irrigation water.....	3,490	3,384	3,060	9,934
20 inches irrigation water.....	3,420	3,490	2,952	9,862
40 inches irrigation water.....	3,567	3,343	2,844	9,754

The soil receiving 5 tons of manure yearly for 12 years had gained 180 pounds in the first foot-section, 72 pounds in the second, and 108 in the third, making a total gain of 360 pounds of total phosphorus. The manure carried to the soil during this time approximately 184 pounds. The irrigation water could have carried to the soil 12 pounds, making a total of 196. This is 154 pounds less than the noted gain due to the difference in the specific plats at the beginning of the experiment.

The plats which received yearly 15 tons of manure per acre gained in the first, second, and third foot 360, 144, and none, respectively, which is 55 pounds less than the quantity applied in the manure and irrigation water. This in part may be due to a difference in the original composition between the different plats which can be ruled out by later analyses on these specific plats. It is evident that the greater quantities of the added phosphorus remain in the surface foot, but probably would be carried deeper if applied with organic manures than if applied as a commercial fertilizer. In the former case the organic and inorganic acids generated from increased bacterial activities would tend to keep greater quantities of phosphorus in solution. Hence, the loss before the third foot-section would be larger.

The total quantity found in the soil, varies inversely with the water. The non-irrigated soil contains 72 pounds more than the soil receiving 20 inches of irrigation water, which is a loss of 6 pounds annually. The soil receiving 40 inches of irrigation water annually shows a loss of 180 pounds, or an annual loss of 15 pounds to the acre. That is, assuming that the plats originally contained the same quantity of phosphorus, which is not certain, the loss due to irrigation water is appreciable and increases with the water applied.

On account of the manure applied, the heaviest concentration of phosphorus is found in the surface section, as is shown in table 5.

TABLE 5  
*Total phosphorus in first, second, and third foot-sections*

TREATMENT	FIRST FOOT	SECOND FOOT	THIRD FOOT
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
No manure.....	35.1	34.4	30.5
5 tons manure.....	35.7	33.8	30.5
15 tons manure.....	36.5	33.6	29.7
No irrigation water.....	34.6	34.1	30.8
20 inches irrigation water.....	34.7	35.4	29.9
40 inches irrigation water.....	36.6	34.3	29.2

TABLE 6  
*Acid-soluble CaO in the various foot-sections and after receiving various manure and water treatments*

TREATMENT	POUNDS PER ACRE OF ACID-SOLUBLE CaO			
	First foot	Second foot	Third foot	Total
No manure.....	575,640	564,480	688,320	1,828,440
5 tons manure.....	565,920	573,120	654,120	1,793,160
15 tons manure.....	563,400	592,560	599,400	1,755,360
No irrigation water.....	569,880	580,680	611,640	1,762,200
20 inches irrigation water.....	566,640	589,320	659,160	1,815,120
40 inches irrigation water.....	568,440	568,800	670,680	1,807,920

It is interesting to note that in the unmanured soil there is a difference of 0.7 per cent between the first and the second foot and a difference of 4.6 per cent between the first and the third. The soil which had received 5 tons to the acre annually has a difference of 1.9 per cent between the first and second and 5.2 per cent between the first and the third feet. The soil which had received 15 tons of manure annually had 2.9 per cent more in the first than in the second, and 6.8 per cent more in the first than in the third foot, showing that there is a tendency for the phosphorus of the manure to concentrate in the first foot-section.

The high calcium content of this soil causes the phosphorus of the organic manure as fast as it is mineralized, due to bacterial activity, to be precipitated as the practically insoluble tricalcium phosphate; hence its concentration in the surface foot-sections.

A composite sample of this soil taken in 1900 yielded 607,680, 640,800, and 768,250 pounds to the acre of acid-soluble calcium oxide in the first, second, and third foot-sections. Assuming that this represented the composition of these specific plats in 1900, we find that the unmanured soil was losing annually 1393 pounds to the acre of calcium oxide from the first acre-foot, 3318 pounds from the second, and 3475 pounds to the acre from the third foot-section. The first foot of this soil is therefore losing approximately the quantity being lost from the Broadbalk field at Rothamsted where minerals and ammonium salt are being added, but is considerably higher than is the average loss from Rothamsted (11).

However, these results are different from the Rothamsted results in that there is an unmistakable loss of lime from the first foot-section due to the use of barnyard manure. This excessive loss, where 5 tons to the acre was applied, is 81 pounds of calcium oxide yearly; where 15 tons to the acre was applied the annual loss was 120 pounds. The 3 feet register an annual loss of 2940 pounds where 5 tons to the acre was applied and over twice this quantity where 15 tons to the acre annually was applied. This is the minimum loss of calcium from this soil, for the manured soils are receiving each year the calcium of the manure which disappears in addition to the above reported quantities. While the probable differences in the composition of these plats at the beginning of the experiment may account for some of this difference, yet the uniformity of the results makes it certain that this is not the only factor and that the manure is rendering soluble the calcium, and hence hastening its removal by the irrigation water from the surface of this soil.

The first foot-section shows an annual loss of 270 pounds due to 20 inches of irrigation water and only 120 where 40 inches of irrigation water was applied. The 3-foot section shows an annual gain of 4410 pounds where 20 inches of water was applied and 3810 pounds to the acre where 40 inches of irrigation water was applied. This gain would come primarily from the water carrying to the surface the soluble calcium salts, as the 20 inches of irrigation was carrying 231 pounds annually to the soil and the 40 inches, 462 pounds (8). The irrigated and non-irrigated soil is receiving the same quantity of calcium in the manure; hence, it could not come from this source. There is also the possibility that the irrigation water has increased the quantity of acid-soluble calcium from the insoluble store of the soil. However, this would probably be small.

In view of the great care used in taking and analyzing these samples, a number of years hence an accurate measurement of the loss and gain of the various constituents can be obtained. Tentatively, it can be accepted that this soil is losing 1400 pounds of calcium oxide annually and that this is greatly increased by the application of organic manures, but is not greatly influenced by the application of irrigation water when it does not exceed 40 inches annually.

As an average, 31.7 per cent of the calcium in the three foot-sections is in the first foot, 32.3, in the second, and 36.1 in the third. The percentage in the first and second foot-section increases on account of manure, and decreases in the third foot-section, whereas irrigation water causes a decrease in the first and second and an increase in the third foot-section. It is therefore evident that both manure and irrigation disturb the relative distribution of the calcium in the surface 3 feet of soil to a greater extent than they do the total nitrogen (10).

The acid-soluble magnesium is given in table 8.

TABLE 7

*Total calcium in first, second and third foot-sections of soil receiving varying quantities of water and manure*

TREATMENT	FIRST FOOT	SECOND FOOT	THIRD FOOT
No manure.....	31.5	30.9	37.7
5 tons manure.....	31.6	32.0	36.5
15 tons manure.....	32.1	33.8	34.1
No irrigation water.....	32.3	32.9	34.7
20 inches irrigation water.....	31.2	32.5	36.3
40 inches irrigation water.....	31.4	31.5	37.1

TABLE 8

*Acid-soluble magnesium oxide in the various foot-sections of soil receiving varying quantities of manure and irrigation water*

TREATMENT	POUNDS PER ACRE OF ACID-SOLUBLE MAGNESIUM OXIDE			
	First foot	Second foot	Third foot	Total
No manure.....	399,600	387,000	427,680	1,214,240
5 tons manure.....	380,160	386,280	404,640	1,171,080
15 tons manure.....	376,200	390,600	387,720	1,154,520
No irrigation water.....	385,560	379,800	398,880	1,164,310
20 inches irrigation water.....	383,400	397,080	423,360	1,203,840
40 inches irrigation water.....	387,360	387,000	410,040	1,184,400

The magnesium, like the calcium, is more concentrated in the second and third foot-sections than in the first. The excess annual loss from the 5-ton manured plats was 1620 from the first foot, 60 pounds from the second, and 1920 from the third. The plat receiving annually 15 tons of manure per acre had an excess annual loss over that of the unmanured plat of 1950 for the first foot, 3330 for the third, and a gain of 300 pounds annually from the second foot. In addition to this, there is the loss of magnesium which is being brought to the manured plats in the farm manure. Hence, the loss is actually higher than reported. Therefore, the organic manure is hastening the loss of magnesium from the soil and this to a greater extent than is the case with the calcium. If relatively the same amount of magnesium has been carried from



the soil, as has been the case with the calcium, the use of organic manures will tend to widen the calcium-magnesium ratio in this soil.

The magnesium is more evenly distributed throughout the three foot-sections and although it is more soluble than the calcium salts and is leached from the soil faster than is the calcium, the manure and irrigation water influence but slightly the relative quantity found in the various foot-sections. In this regard it acts very similarly to the nitrogen of the soil, as may be seen by a comparison with previously published results (10).

The calcium-magnesium ratio for the various treatments in the three foot-sections is given in table 10.

TABLE 9

*Total magnesium of the three foot-sections in the first, second, and third foot-sections of soil receiving varying quantities of irrigation water and manure*

TREATMENT	FIRST FOOT	SECOND FOOT	THIRD FOOT
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
No manure. ....	32.9	31.9	35.2
5 tons manure. ....	32.5	32.9	34.5
15 tons manure. ....	32.6	33.8	33.6
No irrigation water. ....	33.1	32.6	34.2
20 inches irrigation water. ....	31.9	32.9	35.2
40 inches irrigation water. ....	32.7	32.7	34.6

TABLE 10

*Ratio of calcium to magnesium in soil receiving varying quantities of water and manure*

TREATMENT	CaO:MgO IN VARIOUS FOOT-SECTIONS		
	FIRST FOOT	SECOND FOOT	THIRD FOOT
No manure. ....	1.44	1.46	1.61
5 tons manure. ....	1.49	1.48	1.62
15 tons manure. ....	1.50	1.52	1.55
No irrigation water. ....	1.44	1.53	1.53
20 inches irrigation water. ....	1.48	1.48	1.56
40 inches irrigation water. ....	1.47	1.47	1.64

The widest ratio of calcium to magnesium in the first foot of soil is where 15 tons of manure had been applied, and the narrowest is where no manure was received by the soil. The application of manure to a soil widens the ratio in the first and second foot-sections, whereas it narrows it in the third foot-section. The application of water also widens the calcium-magnesium ratio, as would be expected from the solubility of calcium carbonate and magnesium carbonate. Viewed in the light of the results of Furuta (2) this soil at present should be best adapted to crops such as cereals, whereas in time, as the ratio widens, it should be adapted to crops with heavier foliage. However, the quantity of each constituent soluble in the soil solution would be of more importance than the total salts in the soil (16). Viewed in this light this

soil at the present time has a calcium-oxide-magnesium-oxide ratio of 1.2:1.0 (9). However, we are probably dealing in this soil with a double salt of calcium and magnesium  $[\text{CaMg}(\text{CO}_3)_2]$  which undoubtedly would modify the toxicity of magnesium.

A highly calcareous soil, to which 5 tons of barnyard manure had been applied yearly for 12 years, had stored within it at the end of this period 17.7 per cent of the organic material which had been applied. Similar soil receiving 15 tons of manure annually had retained 71.4 per cent of the applied organic carbon.

The manured soil decomposed approximately 3000 pounds of organic carbon yearly over that decomposed in unmanured soil. This was nearly the same with heavy and light applications of barnyard manure.

#### SUMMARY

Because of the great care which has been exercised in the collecting and analyzing of these samples, in the future an exact inventory of the carbon, calcium, magnesium, and phosphorus transformation of these irrigated and manured plats can be obtained. Tentatively, the following conclusions can be drawn from the work done to date.

The application of manure to this soil tends to widen the carbon-nitrogen ratio, whereas irrigation water narrows it.

The phosphorus applied to the soil was found distributed in the first, second, and third foot-sections, with the greater quantity of it in the first foot-section. The results point to the conclusion that the irrigation water has caused a concentration of the phosphorus in the surface foot-sections which might be otherwise if excessive quantities of water were used.

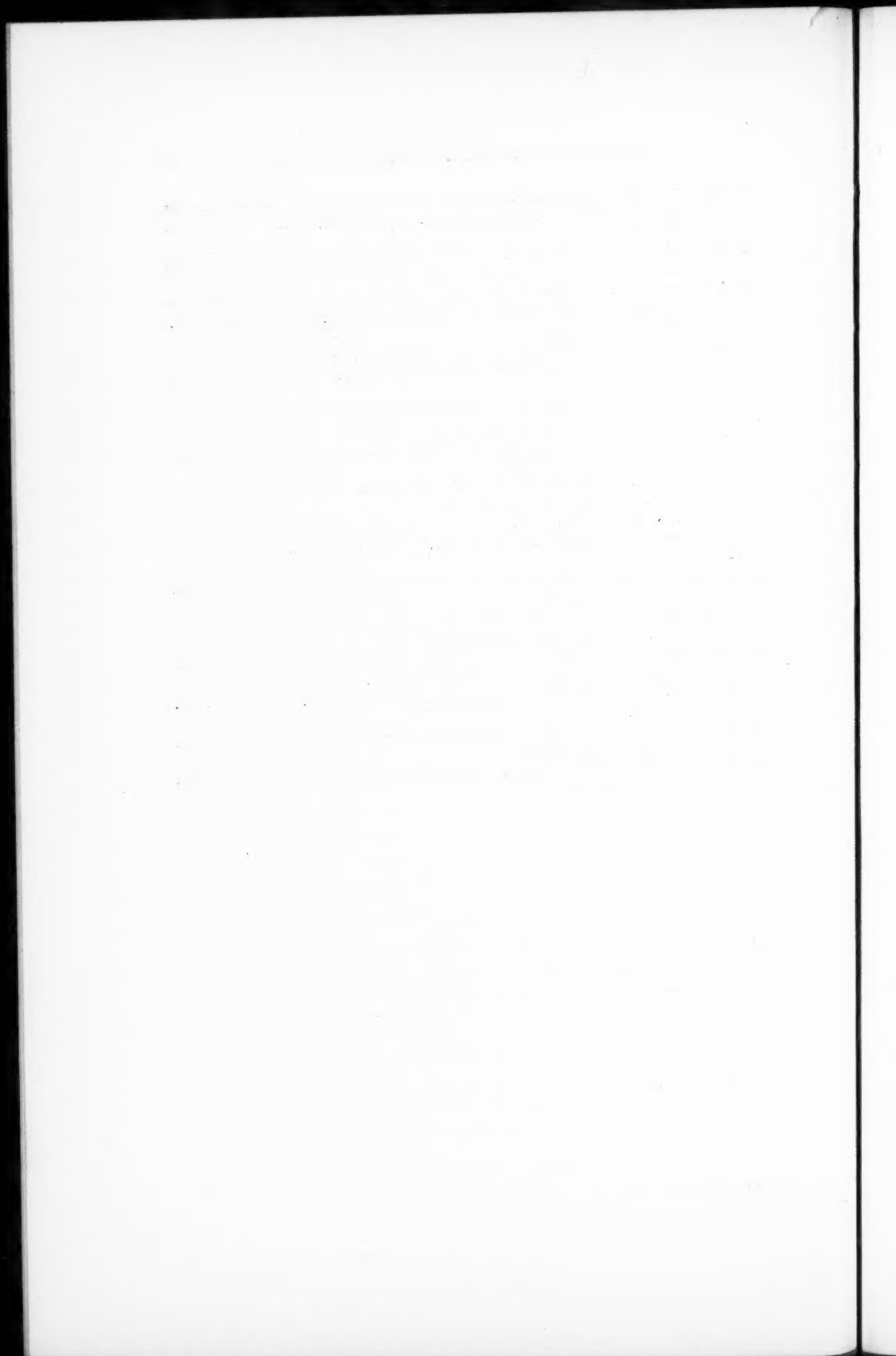
The unmanured soil was losing 1393 pounds per acre of calcium oxide from the first acre-foot, 3318 pounds from the second, and 3475 pounds per acre annually from the third. This loss was increased by manure, but was less as the irrigation water applied increased.

Magnesium carbonate, being more soluble than the calcium carbonate, is being carried from the soil more rapidly than is the calcium carbonate. This also is being rendered more soluble by the organic manure. The percentage distribution within the 3 feet is not greatly changed either by manure or irrigation water. The calcium-magnesium ratio is widened by both organic manure and irrigation water.

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## THE FIXATION OF NITROGEN BY AZOTOBACTER IN A DISPLACED SOLUTION AND IN SOIL RESIDUE THEREFROM

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Experimentation on nitrogen fixation by *Azotobacter* has, until now, been concerned almost exclusively with media very rich in sugars or similar substances. Like so many procedures in the sciences, and particularly in the inexact sciences, the methods of study to which we have just referred have not deviated in principle, in many years, from those originally adopted by the bold pioneer workers in the field. The result has been that, with few well-known exceptions, investigators of the subject have assumed that it is essential to use large quantities of soluble carbohydrates or similar substances of relatively simple and known composition, in order to show the nitrogen-fixing powers of *Azotobacter* or of other organisms. Their results have led them to the conclusion that, thermodynamically speaking, the biological process of nitrogen fixation is a highly inefficient one. Some of us have long suspected, however, that not only should such conclusions be regarded as tentative, but that the development of new methods for the study of the problem would be sure to endow the question with a wholly different aspect. The opportunity for study of the problem by a different method from that in vogue both heretofore and at present seemed to us to present itself in the recent studies of soil solution and particularly of displaced soil solutions. We determined, therefore, to ascertain the extent of nitrogen fixation by pure cultures of *Azotobacter* in a displaced soil solution and in the soil residue from the displacement operation by which that solution was obtained.

### METHOD OF THE EXPERIMENT

We employed a displaced solution and a soil which had accumulated from the extensive studies on displacement carried on by our colleagues Messrs. Burd and Martin. Because the displacements by means of which the solution and soil were obtained had been carried beyond completion, or to the point at which the water which served as the displacing liquid had mingled with the soil solution, our medium was somewhat more dilute than the soil solution characteristic of the soil in question. The latter was a rather poor soil which yielded a solution of relatively low conductivity and freezing-point depression. The solution was clear and slightly yellow. Our plan and procedure was to inoculate thin layers of the displaced solution and the

displaced soil with a suspension of a California strain of *Azotobacter*, to incubate at 28 to 29°C. for 18 days in the case of the solution, and 4 weeks in the case of the soil, and then analyze for total nitrogen. For this purpose, the solution was distributed in 50-cc. portions in 300-cc. Pyrex Erlenmeyer flasks and sterilized and inoculated. The soil was distributed in the same kind of flasks in 50-gm. portions in the moist state in which it was taken from the cylinders used for displacement. In this case, however, one series was inoculated without sterilization of the soil and another only after thorough sterilization. Moisture determinations were made on the soil which showed that each flask contained actually 44 gm. of dry soil (at 100°C.). In order to control the experiment, 6 solution cultures of the same kind were incubated after inoculation and 6 were analyzed immediately after inoculation. In the case of the soil, likewise, 6 cultures were incubated in each of the two sets just described and 4 soil cultures similarly inoculated were immediately analyzed for total nitrogen. The inoculum used throughout consisted of a 1-cc. suspension of a week-old culture of *Azotobacter chroococcum* (Madeira strain) in the usual mannite solution. The soil cultures were kept moist by additions from time to time of sterile distilled water. In making the analyses of the soil cultures, all the soil in every culture and not merely a fraction thereof, was digested and analyzed. The modified Gunning method for total nitrogen was employed throughout. Both the displaced solution and the soil were analyzed for total carbon by the wet combustion method. The results of these analyses are indicated below.

#### OBSERVATIONS AND RESULTS OF THE EXPERIMENT

The soil cultures did not, of course, show any outward signs of the processes operating in them. The solution cultures, however, showed some interesting characteristics in the course of the incubation period. The bacteria developed slowly in them, but developed steadily. Nothing but a very thin, iridescent film was visible at the surface of the thin layer of liquid. At the bottom of the solution, however, and particularly at the center of the flask, a constantly increasing sediment was produced. This gave the appearance of a bottom yeast culture, much more than of an *Azotobacter* culture. There was little or no odor in the cultures. After the incubation periods used in the solution and in the soil cultures respectively, the analyses for nitrogen gave the results indicated in tables 1 and 2.

We may first consider the results of the analyses of the solution cultures given in table 1. Every culture but one of the 6 solution cultures showed after incubation a gain of nitrogen over the similarly treated but sterilized culture solutions. While the gain was not large, it was consistent throughout and, considering the small amount of carbon present in the solution, was all that could be expected. These results show clearly that *Azotobacter* can fix nitrogen with the small amount of carbon available in a weak soil solution. Moreover, the organism can effect that fixation with

an efficient use of the carbon available. Analysis of the solution for total carbon showed that 50 cc. thereof, as used in each culture, contained 8 mgm. of carbon. Adding to this 8 mgm. more for the inoculum from the mannite solution as originally constituted, we find that approximately 40 mgm. of carbon were used in the fixation of 1 mgm. of nitrogen. When this is contrasted with the usual figures for corresponding cultures in sugar solutions or mannite solutions, the difference is instructive. It is well known that the figures obtained in the past with reference to the power of *Azotobacter* to

TABLE 1  
*Nitrogen fixed by Azotobacter chroococcum in displaced soil solution*

CULTURE NUMBER	N FOUND AFTER INCUBATION	N IN STERILE CONTROLS	N FIXED
	mgm.	mgm.	mgm.
1	1.26	0.70	
2	0.84	0.84	
3	0.98	0.84	
4	1.26	0.42	
5	1.12	0.84	
6	1.20	0.84	
Average.....	1.11	0.75	0.36

TABLE 2  
*Nitrogen fixed by Azotobacter chroococcum in displaced soil*

CULTURE NUMBER	IN PURE CULTURES		IN MIXED CULTURES	
	N found after incubation	N found in soil controls	N found after incubation	N found in soil controls
	mgm.	mgm.	mgm.	mgm.
1	25.9	21.1	23.7	21.1
2	25.3		25.5	
3	26.9	23.1	26.2	23.1
4	25.3	23.5	25.1	23.5
5	25.2		24.8	
6	24.9	22.1		22.1
Average N fixed (mgm.)	3.1		2.5	

employ the energy in sugars or mannite, show that for every mgm. of nitrogen fixed, there were used from 70 to 400 mgm. of carbon. Besides, the first figure is given in only one recorded case for pure cultures and is at least twice the efficiency obtained even with the best strains of *Azotobacter*. Moreover, we have allowed very liberally for the carbon content in the inoculum used in our experiment. Since 1 cc. of inoculum was used, we calculated the amount of carbon in 1 cc. of the original sterile mannite solution. Obviously, however, this is too liberal an allowance, since the inoculum was

from a week-old culture of the organism which had unquestionably used in the nitrogen-fixation process most of the carbon in the mannite. In other words, therefore, the opinion may be safely hazarded that a considerably larger efficiency than that indicated by the ratio of 1 mgm. of nitrogen to 40 mgm. of carbon actually characterized the solution cultures of our experiment. Unfortunately, no carbon determination was made on the inoculum itself and hence it is necessary to leave the question of definite degree of efficiency of the fixation process in abeyance for the time. That under the proper conditions, it is astoundingly more efficient than has been assumed in the past is clearly evident. This is the more striking since the forms of organic carbon in a soil solution would never have been assumed by chemists and bacteriologists to be nearly so available as that in a sugar or an alcohol, and that it should be much more efficient seemed generally to be unthinkable. All this makes it certain that *Azotobacter* in a soil solution, however poor in organic carbon, can fix nitrogen with a very high degree of efficiency from the point of view of the returns from a limited amount of energy expended. It is assumed, of course, that it can proceed to the maximum only under propitious environmental conditions, chiefly those of temperature.

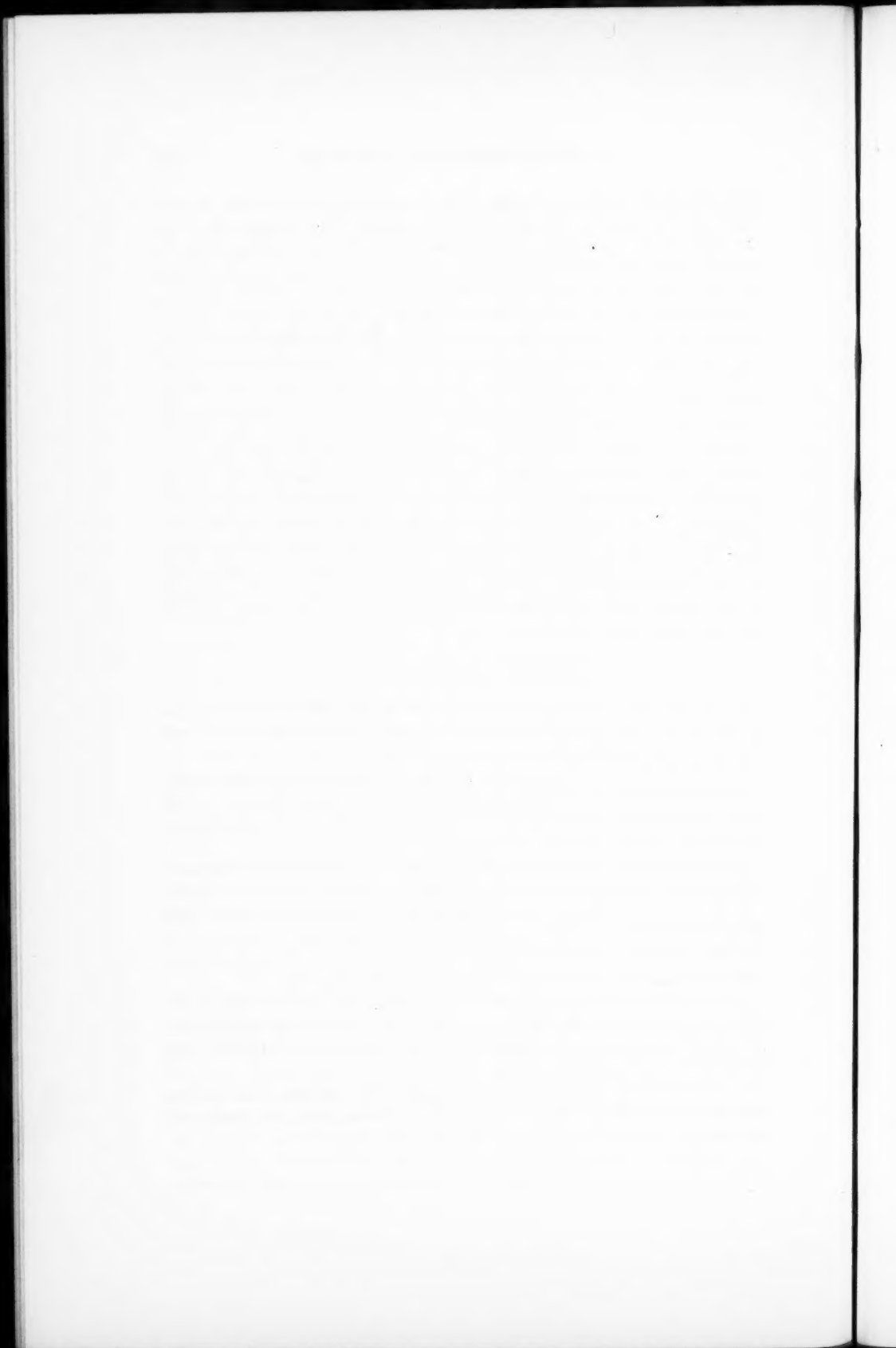
Passing now to a consideration of the soil cultures, we find even more interesting results than in those of the solution cultures, as indicated in table 2. It will be remembered that the soil used was the residue from the displacement process. All of the carbon compounds therein which could become quickly soluble had been removed by displacement and by carrying the process of displacement beyond completion. As above indicated, nothing but relatively insoluble carbon compounds were left. To be sure, the addition of distilled water made it possible for more of the relatively insoluble carbon compounds to go into solution during the incubation period. Such substances in addition to those which the organisms could themselves render soluble, constituted the sole source of carbon for *Azotobacter* in the displaced soil. In spite of that, however, the data in table 2 show in absolute figures much larger fixation of nitrogen than in the soil solution, though relatively the efficiency of the process in the soil cultures is only about one-half as great as in the soil solution. It will be seen from table 2 that on the average from 2.5 to 3.1 mgm. of nitrogen were fixed per culture. Analysis of the soil for carbon shows that every culture contained 200 mgm. of carbon. This would indicate that even with the highest average fixation obtained, about 70 mgm. of carbon were used for the fixation of 1 mgm. of nitrogen. Even this, however, exceeds by far the efficiency usually ascribed to *Azotobacter* in carbon-rich media where the carbon compounds are all soluble; and, curiously enough, the carbon compounds left in a displaced soil like that employed by us would be expected to be largely inert and useless for the work of pure cultures of *Azotobacter*. We speak of pure cultures of *Azotobacter*, because while fixation took place also in the unsterilized soil, the fixation was apparently greater in the soil which was first sterilized and



then inoculated with *Azotobacter*. The foregoing statements may be misleading if one takes literally the word "use" above. The 70 mgm. of carbon per mgm. of nitrogen fixed were present in the soil but certainly were not all used, since they represent the total carbon in a given amount of soil and not that which can be rendered usable in the incubation period in question. Unfortunately, no estimate of the available fraction of that amount of carbon can be made at present, hence we state above, quite arbitrarily we admit, that the fixation of nitrogen by *Azotobacter* is more efficient in the displaced solution than in the displaced soil. It is just as safe to assert that, everything considered, the process in the displaced soil is fully as efficient as, and perhaps more so than, in the displaced solution for reasons which must be obvious to the reader. Otherwise, the data in table 2 speak clearly for themselves. The variability of the soil is indicated in the analyses, as is true of any series of soil samples from any soil, but the differences between the unincubated soils and those incubated, as regards nitrogen content, are definitely outside the limits of variability and of error, as the several analyses show. Even the highest value for the nitrogen content of the control soils which received inoculum like the cultures, is below the lowest value for nitrogen in the cultures, and that lowest value is the only one in the whole series of cultures which is so very low.

#### SUMMARY AND CONCLUSIONS

1. The efficiency of *Azotobacter chroococcum* at nitrogen fixation in a displaced soil solution was determined without addition of carbohydrate except that in 1 cc. of inoculum from a mannite culture.
2. Such efficiency far exceeds that obtained in rich sugar or alcohol media.
3. The efficiency of *Azotobacter chroococcum* at nitrogen fixation in soil whose solution has been displaced and without addition of carbohydrate except that in the inoculum, was determined.
4. Such efficiency, while not apparently so great as that in the displaced solution, was much greater than that in solutions rich in sugars or alcohols.
5. In such soil cultures, *Azotobacter* is more efficient when alone than when it is allowed to work in a previously unsterilized soil.
6. The efficiency of nitrogen fixation by *Azotobacter* in the displaced solution is greater than 1 mgm. of nitrogen per 40 mgm. of carbon.
7. The efficiency of nitrogen fixation by *Azotobacter* in the displaced soil is greater than 1 mgm. of nitrogen per 70 mgm. of carbon if the total carbon in the soil is included in the computation. It must be much higher if only the available carbon is considered.
8. These findings may give a new lease of life to the old idea of inoculating soils with *Azotobacter*. They certainly give a new aspect to the question of the relative efficiencies of bacterial nitrogen-fixation processes.



## THE AVAILABILITY OF SUBSOIL POTASH

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Most studies relating to the amount and condition of plant-food in the soil have confined themselves to the surface horizon. Relatively few studies have been made of soils from lower horizons. In humid regions it is, indeed, generally assumed that the plant-food of the subsoil is raw and unavailable, and not in a condition to support a thrifty plant growth. That this general assumption may be unsound is shown by the work of Alway, McDole and Rost (1), who found that the subsoils of the loess soils of Nebraska, while indeed typically "raw" toward non-legumes, were quite the reverse toward inoculated legumes. This fact indicates nitrogen as the factor limiting growth in subsoils brought to the surface, and likewise indicates other nutrients as being present in available form and in quantities sufficient for good plant growth.

Harmer (3, p. 401) working with glacial subsoils in humid Minnesota, found that "some of the glacial subsoils are as productive of alfalfa as surface soils when inoculation is assured, but others are quite unproductive, and the rawness is not associated with an especially low nitrogen content or with a lack of carbonates." McMiller (7), following out the work of Harmer, showed that "an application of soluble potash and phosphoric acid fertilizers removes this infertility, rendering the subsoils as productive as the corresponding surface soils, evidence that 'rawness' in these cases is due to a lack of readily available mineral nutrients." It is evident that even in humid regions subsoils brought to the surface are not always unproductive, and that when unproductive this condition may be due to several factors.

The work reported in this article was outlined and carried through by former Director William P. Brooks, and confined itself to a study of the availability of subsoil potash, as determined by means of culture tests. The work as outlined contemplated an attempt to make use of potash reserves in the deep subsoils through use of deep-rooted crops in the planting system, and portrayed an expectation that the subsoil would be relatively unproductive. This expectation was not realized. Unfortunately it has not yet been possible for the station to undertake the field studies originally planned. Work already reported (4) shows a rather serious potash deficiency in a soil very closely related to that under study, namely, one of the Merrimac series.

## METHODS

Bulk samples of soil from 5 different horizons, surface soil, and first, second, third and fourth feet of subsoil, respectively, were taken from a field classified in the soil survey as Hartford fine sandy loam. A physical analysis of the soil of the different horizons at the beginning of the experiment in 1914, and a determination of the acid-soluble potash were made, as follows:

	SURFACE SOIL	FIRST FOOT SUBSOIL	SECOND FOOT SUBSOIL	THIRD FOOT SUBSOIL	FOURTH FOOT SUBSOIL
Mechanical analysis of soil passing 1-mm. sieve:					
Loss on ignition . . . . .	5.02	1.31	3.42	3.51	4.13
Coarse sand, 1.0-0.5 mm. . . . .	0.45	3.12	14.34	24.34	19.57
Medium sand, 0.5-0.25 mm. . . . .	1.26	4.45	10.78	13.15	15.43
Fine sand, 0.25-0.1 mm. . . . .	6.00	24.38	22.61	5.50	13.20
Very fine sand, 0.1-0.05 mm. . . . .	50.44	48.10	18.02	21.68	19.20
Silt and fine silt, 0.05-0.005 mm. . . . .	34.05	17.14	22.16	11.82	10.96
Clay, less than 0.005 mm. . . . .	2.78	1.50	8.67	20.00	17.51
Percentage of acid-soluble potash in soil passing 1-mm. sieve (dry matter basis).	0.235	0.270	1.174	1.733	1.97

Later an analysis was made of the acid-soluble potash in a composite sample representing the soils used in the first 3 years of the investigation, with the following results:

	<i>per cent</i>
Surface soil. . . . .	0.242
First foot subsoil. . . . .	0.262
Second foot subsoil. . . . .	0.474
Third foot subsoil. . . . .	1.081
Fourth foot subsoil. . . . .	1.296

The magnitudes of the acid-soluble potash in the soils of the first year are in the same order as those in the composite sample of 3 years. A detailed analysis of results shows, however, that despite the attempt to secure approximately the same soil year by year, there was a significant variation. On account of the shortage of help brought about by war conditions, further physical and chemical measurements of these soils were not made. These failures must be considered as errors in experiment. The fact that the high potash concentration of the lower soil horizons is accompanied by an increase in clay content at the expense of the coarser grades of soil particles, as indicated by the physical analysis of 1 year only, may be of considerable importance in interpreting the significance of the results which follow.

The soils from each horizon were arranged in 4 series of vegetation tests, receiving differential treatment as indicated:

- Series 1, normal—no treatment other than that also given to other series.
- Series 2, lime.

Series 3, prepared humus.

Series 4, humified straw.

The fertilizer treatment per culture was as follows:

	1914	1915-1918
	<i>grams</i>	<i>grams</i>
Nitrate of soda . . . . .	2.2	2.5
Sulfate of ammonia . . . . .		2.0
Dried blood . . . . .	3.0	3.0
Hoof meal . . . . .		28.0
Acid phosphate . . . . .	9.0	9.0

It will be noted that an attempt was made to fertilize the different pots with an excess of phosphorus and nitrogen, in the expectation that potash would then be the limiting nutrient element. The increase in the quantity of nitrogen applied in 1915 and later was due to the relatively small yields secured in 1914. The weights of dry soil used per culture were as follows:

	1914	1915	1916	1917	1918
	<i>kgm.</i>	<i>kgm.</i>	<i>kgm.</i>	<i>kgm.</i>	<i>kgm.</i>
Surface soil . . . . .	16.0	16.5	16.5	15.5	15.5
First foot subsoil . . . . .	16.0	18.5	20.5	17.5	18.5
Second foot subsoil . . . . .	18.5	21.5	20.0	18.0	19.0
Third foot subsoil . . . . .	20.5	19.5	18.5	19.0	18.5
Fourth foot subsoil . . . . .	20.5	18.5	18.5	19.0	18.5

These pots were of zinc, of the Wagner type, 10 inches in diameter, and so arranged that watering could be from both the bottom and the top.

Japanese barnyard millet was grown in duplicate cultures in each series, without added potash, with 2 gm. per culture of muriate of potash (equivalent to 1 gm. of actual potassium oxide), and with 4 gm. of muriate of potash, respectively; the 2-gm. treatment being omitted the first year. Results were measured in terms of total dry matter produced, and in concentration of potash.

Table 1 shows the average yields expressed in terms of the above-mentioned units of measurement. Notation is also made as indicated, showing conditions under which a given result is not comparable with others having the same number of years in the general average.

Unfortunately the accidents to which work of this kind are always subject were such that the averages are in many cases incomparable. In all tables except the first, data which are not comparable have been omitted. While it is unfortunate that in most cases the surface soil comparisons are thus made impossible, there seems no other way in which interpretation of these data may be made.

Mere inspection of the data in table 2 shows that the expectation of the subsoil being relatively unproductive was not realized. A yield of 100 gm. of dry matter per culture is equivalent to a yield of about 10,000 pounds of dry

TABLE 1  
Yield of dry matter and concentration of potash—Summary by soils, averages

SOIL HORIZON	TREATMENT	NO POTASH				2 GRAMS MURIATE OF POTASH				4 GRAMS MURIATE OF POTASH			
		Years in average	Average number of plants per culture	Dry matter	Concentration of potash	Years in average	Average number of plants per culture	Dry matter	Concentration of potash	Years in average	Average number of plants per culture	Dry matter	Concentration of potash
				grams	per cent			grams	per cent			grams	per cent
Surface soil	Normal	5	3.90	101.39	1.55	4	3.75	107.80	1.94	5	4.40	106.84	1.99
	Lime	4	4.75	104.72	1.59	4*	4.10	101.77	1.93	4	5.00	112.11	1.99
	Humus	5	4.00	134.78	1.70	4	4.10	125.32	2.21	5†	4.30	137.32	2.05
	Straw	4*	4.70	130.28	2.05	3	4.80	125.90	2.29	3	5.00	134.83	2.32
First foot sub-soil	Normal	5	5.00	108.13	0.97	4	4.90	127.64	1.25	5	5.00	121.52	1.73
	Lime	5	5.00	86.93	1.18	4	4.90	103.65	1.42	5	4.90	98.80	1.70
	Humus	5	5.00	144.31	1.05	4	5.00	145.84	1.33	5	5.00	156.03	1.61
	Straw	4*	5.00	135.15	1.92	3	5.00	145.28	1.90	4	4.90	159.27	2.18
Second foot subsoil	Normal	5	5.00	121.53	1.16	4	5.00	146.72	1.42	5	4.80	127.13	1.72
	Lime	5	5.00	98.60	1.25	4	4.50	117.06	1.62	5	4.90	105.86	1.89
	Humus	4	4.90	149.04	1.63	3	4.80	157.61	2.01	4	4.75	145.84	2.14
	Straw	4	5.00	163.46	1.82	4	5.00	161.48	2.09	3‡	5.00	150.31	2.05
Third foot subsoil	Normal	5	5.00	101.47	1.70	4	5.00	113.55	1.89	5	5.00	103.40	2.00
	Lime	5	5.00	77.69	1.89	4	5.00	86.53	2.12	5	5.00	74.85	2.24
	Humus	5	5.00	130.86	1.64	4	5.00	127.54	2.00	5	4.90	130.92	2.16
	Straw	4	5.00	144.48	2.12	3	5.00	157.81	2.16	4	5.00	136.25	2.36
Fourth foot subsoil	Normal	5	5.00	92.39	2.29	4	5.00	104.53	2.32	5	5.00	89.31	2.39
	Lime	5	5.00	75.02	2.19	4	5.00	87.76	2.34	5	5.00	76.69	2.37
	Humus	5	5.00	137.38	2.24	4	4.90	126.30	2.55	5	4.80	132.73	2.46
	Straw	4	5.00	125.46	2.45	4*	5.00	121.92	2.57	4	5.00	120.29	2.59

\* Seven cultures.

† Nine cultures.

‡ Five cultures.

TABLE 2  
Yield of dry matter and potash, and concentration of potash in dry matter: series I, no potash, 1914-1918, inclusive

SOIL HORIZON	NUMBER OF YEARS IN AVERAGE	AVERAGE NUMBER OF PLANTS PER CULTURE	DRY MATTER PER CULTURE	CONCENTRATION OF POTASH	YIELD OF POTASH IN DRY MATTER
			grams	per cent	grams
Surface soil.....	5*	4.75	110.55	1.54	1.702
Subsoil 1.....	5	5.00	108.13	1.01	1.092
Subsoil 2.....	5	5.00	121.53	1.22	1.483
Subsoil 3.....	5	5.00	101.47	1.85	1.877
Subsoil 4.....	5	5.00	92.39	2.26	2.088

\* Eight pots only.



matter per acre, based on the ratio of soil used in the different cultures compared to the weight of surface soil of an acre (estimated as being 2,000,000 pounds).

Whether the availability of the potash in these soils may best be judged by the concentration of potash in dry matter, or by the total yield of potash in the above-ground parts, is a debatable question. Regardless of method it is apparent that both the concentration and the total recovery of potash are very much lower in the first foot of subsoil than in the surface soil in the fourth foot of subsoil. Without exception there is decreased concentration of potash in dry matter in the first foot of subsoil as compared with the surface soil, and with one exception consistent increased percentage of potash in the second, third and fourth horizons. The conclusion seems warranted that there is either a lower amount of potash in the first foot of subsoil than in the deeper soil horizons, as indicated by chemical analysis; or that the potash in those horizons is much less available than that in the deep subsoil. Whether or not this is due to concentration of clay and silt in the deep subsoil is a question which data recorded do not adequately answer.

From table 3 certain deductions may be drawn, as follows:

1. There is no significant effect of the addition of potash on yield of dry matter, excepting when applied on subsoil 1. Analysis by Student's formula of the data making up the averages of this horizon shows for normal, unlimed soil, odds of 51 to 1 that increase in yield due to the application of 2 gm. of muriate of potash is significant; and odds of 86.7 to 1 that the application of 4 gm., compared with no potash, has produced a significant increase in the yield of total dry matter. The same estimates for the limed series, subsoil 1, show odds of 5 to 1 and 9 to 1 respectively. Mere inspection of the data for the other 3 subsoils shows that there is no significant increase in yield.

2. In each potash treatment there is a regular and consistent increase in concentration of potash from one subsoil horizon to a deeper, culminating in an astonishingly high concentration at the deepest horizon.

3. There is a regular and entirely consistent increase in concentration from no potash through the 2-gm. application to the 4-gm. application, with the single exception of the deepest horizon, at which depth all cultures seem to have taken up a maximum of potash and to be practically independent of further application as far as concentration in dry matter is concerned. Application of Student's formula, comparing the no-potash treatment with the 4-gm. treatment, shows the following significant odds in favor of difference in potash concentration in the dry matter.

	NORMAL	LIMED
Subsoil 1.....	322 to 1	131 to 1
Subsoil 2.....	118 to 1	87 to 1
Subsoil 3.....	62 to 1	28 to 1
Subsoil 4.....	4 to 1	3 to 1

#### EFFECT OF LIME

Hydrated lime was used. In 1914 and 1918 it was applied at the rate of 12 gm. per pot; in 1915, 1916 and 1917, at the rate of 24 gm. per pot. The second part of table 3 gives the data resulting from its use.

For some unexplained, and we fear unexplainable reason, lime in the quantities applied decreased yield. On the other hand, there is a measurable and rather consistent increase in concentration of potash in those cultures receiving

TABLE 3  
*Influence of added potash, average per culture, 1915-1918, inclusive*

SOIL HORIZON	NO POTASH		MURIATE OF POTASH, 2 GRAMS		MURIATE OF POTASH, 4 GRAMS	
	Dry matter	Potash in dry matter	Dry matter	Potash in dry matter	Dry matter	Potash in dry matter
	grams	per cent	grams	per cent	grams	per cent
<i>Series I, normal</i>						
Subsoil 1.....	120.26	0.94	127.64*	1.25	135.82	1.68
Subsoil 2.....	142.25	1.14	146.72	1.42	147.02†	1.69
Subsoil 3.....	118.67	1.68	113.55	1.90	120.02	2.00
Subsoil 4.....	107.34	2.31	104.53	2.32	104.54	2.42
<i>Series II, lime</i>						
Subsoil 1.....	94.25	1.15	103.65*	1.42	107.42*	1.65
Subsoil 2.....	113.97	1.24	117.06†	1.62	122.77	1.86
Subsoil 3.....	88.61*	1.90	86.53	2.12	84.25	2.27
Subsoil 4.....	86.06	2.22	87.76	2.34	88.48	2.41

*Note:* The average number of plants per culture was 5, except as indicated:

\* One pot of the 8 had only 4 plants.

† Two pots had 4 plants each, 1 pot had only 3 plants.

‡ Two pots of the 8 had only 4 plants.

lime, as compared to the analogous cultures receiving no lime, up to the deepest horizon. At this point, concentration in potash seems to have reached a maximum, and added lime has no apparent effect. Calculation shows, however, that lime did not increase the total recovery of potash.

#### EFFECT OF PREPARED HUMUS

The amounts of the prepared humus applied year by year to the different cultures, and the amounts of potash in the humus applied were as follows:

SOIL HORIZON	1916		1917		1918	
	Humus	K <sub>2</sub> O	Humus	K <sub>2</sub> O	Humus	K <sub>2</sub> O
	grams	grams	grams	grams	grams	grams
Surface soil.....	400	2.68	400.0	0.56	400	2.70
Subsoil 1.....	80	0.54	128.8	0.18	117	0.79
Subsoil 2.....	800	5.36	400.0	0.56	400	2.70
Subsoil 3.....	80	0.54	128.8	0.18	117	0.79
Subsoil 4.....	800	5.36	400.0	0.56	400	2.70

*Note:* The percentages of moisture in the prepared humus as applied in the 3 years were as follows: 1916, 15.25 per cent; 1917, 22.37 per cent; 1918, 14.5 per cent.

The prepared humus used in 1916 and 1918 was from the same lot; that used in 1917 was from a different lot. While the percentage of potash in this prepared humus was very small, the total per culture was sometimes very large. This fact makes it impossible to measure the influence of organic matter on the availability of subsoil potash. The data, in as far as a comparable series may be presented, may, however, add to our knowledge of luxury consumption of potash; and the comparison between one subsoil horizon and another may confirm or refute tentative conclusions drawn from other series. These data are, therefore, presented in table 4.

TABLE 4  
*Effect of prepared humus, 1916-1918, inclusive*

	NO POTASH		2 GRAMS MURIATE OF POTASH		4 GRAMS MURIATE OF POTASH	
	Normal	Humus	Normal	Humus	Normal	Humus
Subsoil 1:						
Dry matter, grams.....	124.89	142.79	130.39	142.42	137.92	151.99
Potash, per cent.....	1.07	1.22	1.35	1.47	1.79	1.79
Subsoil 2:						
Dry matter, grams.....	133.87	154.64	138.13	157.61	141.38	146.73
Potash, per cent.....	1.22	1.74	1.55	2.01	1.74	2.33
Subsoil 3:						
Dry matter, grams.....	116.63	122.66	110.95	124.91	118.77	124.78
Potash, per cent.....	1.65	1.73	1.73	1.85	1.94	2.09
Subsoil 4:						
Dry matter, grams.....	117.31	133.13	111.74	125.25	112.61	124.36
Potash, per cent.....	2.33	2.49	2.32	2.51	2.42	2.53

Be the cause what it may, applications of this prepared humus produce a consistent and significant increase in the concentration of potash in the dry matter. Variation in the amounts of humus applied to different subsoils makes impossible strict comparison of the data in table 4 with the foregoing. Indications are rather strong, however, that increase in potash concentration, apparently brought about by the application of the humus product, is due to the potash contained in this product rather than to the effect of organic decomposition.

#### EFFECT OF HUMIFIED STRAW

Oat straw was prepared by cutting, moistening with water, and allowing it to stand in a warm room until it became decomposed. Analysis of the straw, as made in 1917 and 1918, follows:

	1917	1918
	per cent	per cent
Moisture.....	86.66	84.80
Potassium oxide.....	0.12	0.09
Nitrogen.....	0.07	0.15

The amounts applied per culture, together with the amounts of potash contained, were as follows:

SOIL HORIZON	1917		1918	
	Straw	K <sub>2</sub> O	Straw	K <sub>2</sub> O
	grams	grams	grams	grams
Surface soil.....	750	0.9	660	0.594
Subsoil 1.....	750	0.9	660	0.594
Subsoil 2.....	750	0.9	330	0.297
Subsoil 3.....	750	0.9	660	0.594
Subsoil 4.....	750	0.9	330	0.297

Results from the use of humified straw are comparable for 1917 and 1918. Here again, the amount of humified straw used per culture was so large that a significant amount of potash was introduced. Results are given in table 5.

TABLE 5  
*Effect of straw, 1917 and 1918*

	NO POTASH		2 GRAMS MURIATE OF POTASH		4 GRAMS MURIATE OF POTASH	
	Normal	Straw	Normal	Straw	Normal	Straw
Surface soil:						
Dry matter, <i>grams</i> .....	—	120.45	110.54	116.10	126.31	123.23
Potash, <i>per cent.</i> .....	—	1.75	1.90	2.03	1.81	2.11
Subsoil 1:						
Dry matter, <i>grams</i> .....	123.72	—	129.50	141.69	139.41	146.57
Potash, <i>per cent.</i> .....	1.04	—	1.33	1.68	1.64	1.93
Subsoil 2:						
Dry matter, <i>grams</i> .....	125.23	139.64	133.11	144.81	136.45	148.10
Potash, <i>per cent.</i> .....	1.06	1.44	1.42	1.72	1.63	1.88
Subsoil 3:						
Dry matter, <i>grams</i> .....	141.30	140.15	134.75	140.38	142.32	140.54
Potash, <i>per cent.</i> .....	1.47	1.77	1.57	1.94	1.79	2.10
Subsoil 4:						
Dry matter, <i>grams</i> .....	133.10	137.64	127.41	133.34	128.18	124.41
Potash, <i>per cent.</i> .....	2.22	2.43	2.23	2.56	2.38	2.52

They are remarkable in confirming practically all the other results as to the concentration of potash in dry matter in the different soil horizons. They also show a consistent increase in concentration from added potash. No conclusions are warranted as to the effect of this material on the availability of the soil potash.

#### LUXURY CONSUMPTION OF POTASH

The foregoing data show the great extent to which luxury consumption of potash is possible. There is no relationship between yield and concentration of potash in the dry matter. In this respect the data confirm results previously

reported by Jordan (6), by Fraps (2), by Hopkins (5), and in different connections by others. Detailed analysis of the data, not reported here, also shows that the amount of potash taken up, in terms of concentration in dry matter, varied significantly year by year, from causes which it is impossible for us to estimate. Jordan (6) presents data which show much the same thing. It is particularly interesting to note that in Dr. Brooks' work the addition of fertilizer potash in quantities greater than were actually utilized by the plant, as shown in table 6, failed in general to increase concentration of potash in dry matter in the first and second subsoils to a quantity equal to that experienced without potash addition in the deeper subsoils. Apparently the application even of maximum quantities of soluble potash failed to increase the total supply of available potash in the more shallow subsoils to the amount already present in the deeper subsoils.

TABLE 6  
*Yield of potash per culture, normal soil*

SOIL HORIZON	NO POTASH	2 GRAMS MURIATE OF POTASH		4 GRAMS MURIATE OF POTASH	
	Yield	Yield	Increase over no potash	Yield	Increase over no potash
	<i>grams</i>	<i>grams</i>	<i>grams</i>	<i>grams</i>	<i>grams</i>
Subsoil 1.....	1.127	1.593	0.466	2.275	1.148
Subsoil 2.....	1.614	2.077	0.463	2.488	0.874
Subsoil 3.....	1.996	2.152	0.156	2.395	0.399
Subsoil 4.....	2.481	2.427	-0.054	2.527	0.046

# CONCLUSION

If the results of culture tests may be taken as indicative of conditions as they exist in the undisturbed soil; and if the concentration of potash in the dry matter produced, for crops of reasonably uniform size, is an adequate method of measuring the availability of potash in the subsoil; the following conclusions are supported by the evidence presented:

1. That in the subsoils under investigation, as treated with plant-foods other than potash, there was no "rawness" or failure to respond to treatment.
2. That the potash in these soils is sufficiently available to give maximum production.
3. That the potash in the deeper subsoil is either more rapidly available or present in greater quantity than in the more shallow subsoils.

The data presented also confirm the already established fact that the amount of potash in the plant at harvest time may not bear any definite relation to the amount actually required by the plant.

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## ALKALI STUDIES: II. TOLERANCE OF ALFALFA, CORN AND SWEET CLOVER FOR ALKALI IN IDAHO SOILS<sup>1</sup>

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In a recent paper (2) the tolerance of wheat for alkali salts in Idaho soil under certain controlled conditions was reported. In this paper a similar report is made on the tolerance of alfalfa, corn and sweet clover.

In the present investigation the general plan and method of procedure are the same as those previously reported, with the following variations: Large galvanized iron potometers holding 200 to 300 pounds of soil were used instead of 4-gallon jars. The crop was planted in the potometers which were placed in the greenhouse during the winter and were moved to the outside as soon as the weather permitted. The soils were sampled at the beginning of the experiment, and at the end of the cropping season. The potometers were left outside during the second winter to be leached by the winter rains, and then cropped to corn and sweet clover in the third season.

The soils and salt concentrations and the manner of mixing were identical with those used in the wheat treatments. Five cuttings of alfalfa were harvested from the potometers. The first 2 represented crops grown in the greenhouse during the winter; the remaining 3 crops were grown after the potometers were removed from the greenhouse in the spring.

Thirty Grimm alfalfa seeds were planted in each potometer. Records were kept on the percentage of germination, using the average of the control potometers as 100 per cent. Because many of the treatments showed very poor germination, it was necessary to replant with small alfalfa plants. In anticipation of this situation a large number of seeds had been germinated in potometers of untreated soil; and these plants were used to fill the shortage when the plants were from 2 to 4 inches tall. Each potometer was made up to 12 plants, and those having higher germination were reduced to that number. Those dying after the first replanting were again replaced a month later, bringing the number up to 12 plants per potometer. After the second crop growth, the 12 plants became too great a number for the containers, so they were reduced to 5 for each potometer.

In this experiment 4 controls of the untreated soil were used; 2 prepared at the beginning and 2 at the end of the series. For some unknown reason

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TABLE 1  
*Alfalfa tolerance*

NUMBER	TREATMENT			SALT RECOVERY						CROP GROWTH							
	Na <sub>2</sub> CO <sub>3</sub>	NaCl	Na <sub>2</sub> SO <sub>4</sub>	Initial salt recovery			Recovery after alfalfa crops			Germination	Replanted seedlings		Dry matter				
				Na <sub>2</sub> CO <sub>3</sub>	Total equivalent Na <sub>2</sub> CO <sub>3</sub>	NaCl	Na <sub>2</sub> SO <sub>4</sub>	Na <sub>2</sub> CO <sub>3</sub>	Total equivalent Na <sub>2</sub> CO <sub>3</sub>		NaCl	Na <sub>2</sub> SO <sub>4</sub>	Plants living Octo-ber 26	Plants living May 8	Crops 1, 2, 3	Crops 4, 5	Total of 5 crops
per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent		
1	Check			0.000	0.034	0.000	0.002	0.000	0.034	0.000	0.010	100	100	100	100	100	
3	0.20			0.027	0.097	0.000	0.001	0.033	0.091	0.000	0.006	64	100	70	143	109	
5	0.40			0.089	0.161	0.001	0.002	0.085	0.150	0.000	0.006	61	100	92	199	188	
7	0.60			0.135	0.228	0.000	0.000	0.123	0.204	0.000	0.006	32	100	87	105	91	
9	0.90			0.232	0.344	0.000	0.000	0.228	0.310	0.000	0.011	0	100	4	0	0	
11		0.10		0.000	0.037	0.079	0.000	0.002	0.034	0.046	0.002	53	83	100	97	165	
13		0.20		0.002	0.036	0.172	0.001	0.000	0.029	0.169	0.006	17	62	66	55	107	
15		0.40		0.005	0.040	0.348	0.001	0.000	0.028	0.331	0.009	6	33	16	10	11	
17			0.20	0.002	0.042	0.000	0.195	0.002	0.027	0.002	0.206	100	100	96	121	137	
19			0.40	0.000	0.034	0.000	0.345	0.002	0.030	0.000	0.378	52	100	100	95	124	
21			0.60	0.000	0.031	0.000	0.482	0.000	0.027	0.000	0.561	79	100	91	94	94	
23			0.90	0.000	0.032	0.000	0.772	0.000	0.026	0.000	0.752	26	96	87	90	98	
25	0.10	0.10		0.002	0.052	0.085	0.000	0.007	0.046	0.079	0.007	97	100	100	86	75	
27	0.30	0.05		0.054	0.130	0.046	0.000	0.041	0.119	0.041	0.007	70	100	100	110	68	
29	0.10	0.30		0.000	0.045	0.175	0.002	0.005	0.043	0.255	0.008	6	33	21	24	31	
31	0.60	0.10		0.158	0.210	0.096	0.002	0.092	0.163	0.067	0.010	29	67	79	82	76	
33	0.20			0.015	0.083	0.160	0.000	0.024	0.069	0.169	0.007	17	41	45	57	66	
35		0.05	0.20	0.000	0.036	0.055	0.133	0.000	0.138	0.033	0.157	85	100	96	80	71	
37		0.30		0.002	0.034	0.178	0.334	0.005	0.035	0.249	0.096	9	71	62	49	61	
39		0.10		0.000	0.035	0.217	0.508	0.000	0.076	0.089	0.425	49	96	87	75	72	
41		0.10		0.000	0.035	0.098	0.813	0.000	0.020	0.090	0.525	41	79	75	79	80	
43	0.10			0.005	0.046	0.000	0.089	0.002	0.032	0.00	0.109	79	96	96	93	83	

45	0.20		0.024	0.077	0.000	0.149	0.023	0.060	0.000	0.170	76	83	100	87	97	97
47	0.30		0.041	0.106	0.000	0.353	0.044	0.084	0.000	0.275	53	100	67	83	130	142
49	0.20		0.018	0.066	0.000	0.492	0.015	0.051	0.000	0.307	73	100	91	72	75	76
51	0.60		0.160	0.237	0.000	0.094	0.137	0.203	0.003	0.059	23	83	75	90	70	83
53	1.00		0.340	0.433	0.000	0.083	0.062	0.311	0.000	0.080	0	46	4	0	0	0
55	0.05	0.05	0.005	0.046	0.038	0.043	0.008	0.048	0.015	0.026	88	100	87	108	81	98
57	0.10	0.10	0.010	0.057	0.069	0.076	0.011	0.066	0.038	0.062	46	92	91	91	96	91
59	0.40	0.10	0.035	0.087	0.098	0.094	0.040	0.102	0.043	0.087	47	91	66	64	88	82
61	0.40	0.05	0.095	0.146	0.053	0.082	0.090	0.169	0.019	0.048	29	71	33	50	86	73
63	0.60	0.10	0.138	0.210	0.067	0.170	0.115	0.174	0.064	0.123	14	75	29	32	33	34
65	0.40	0.10	0.068	0.128	0.094	0.369	0.067	0.138	0.043	0.219	3	71	29	21	39	32
67	0.20	0.05	0.024	0.071	0.044	0.319	0.024	0.086	0.027	0.355	29	83	54	44	64	58
69	0.20	0.05	0.024	0.068	0.051	0.683	0.024	0.062	0.023	0.590	14	96	33	17	25	24
71	0.05	0.20	0.002	0.034	0.055	0.579	0.005	0.040	0.027	0.515	53	100	92	58	79	72
73	1.00	0.05	0.310	0.406	0.051	0.115	0.229	0.296	0.036	0.095	0	33	8	0	0	0
75	0.40	0.10	0.065	0.124	0.095	0.485	0.027	0.096	0.083	0.551	3	70	16	11	5	9
77	0.30	0.20	0.044	0.103	0.176	0.180	0.019	0.109	0.183	0.217	26	57	50	25	38	33
79	0.10	0.20	0.005	0.042	0.185	0.174	0.005	0.043	0.126	0.178	61	96	75	32	64	52
81	0.10	0.40	0.010	0.052	0.278	0.082	0.007	0.049	0.146	0.068	0	42	25	9	19	15

the first 2 were much better than the last 2 controls. The crops, however, on each pair of controls agreed quite closely. The crop on control potometer no. 1 became unusually strong and growthy, and was not considered in calculating the control average for the last 2 cuttings.

Table 1 contains the alkali analyses, including the original salt additions, the initial analyses, and the recovery after 5 cuttings of alfalfa had been grown, calculated as per cent of anhydrous soil. The yield of crops is expressed as percentages of the average of duplicate pots, using the average of the checks as 100 per cent. Germination percentages are expressed in a similar manner.

#### EFFECT OF ALKALI TREATMENTS ON GERMINATION OF ALFALFA

Very low concentrations of single salts have a decided effect on germination. Sodium carbonate when present in a soil alone in a concentration of 0.15 per cent shows a retarded germination, 0.35 completely inhibits, while 0.22 per cent shows very poor germination. Sodium chloride recovery of 0.075 per cent reduced germination 50 per cent, and 0.16 per cent almost entirely prevented germination. The sodium sulfate is less toxic, permitting good germination with concentration as high as 0.48 per cent of recoverable salt. A recovery of 0.77 per cent practically inhibits growth. Sodium chloride is the most toxic of the three salts used, and shows decided toxicity even in the lowest amount added.

Each salt maintains the same characteristic effect on germination throughout the various combinations where it is the predominating salt in the combination.

Small quantities of salts are much less toxic to the plants in the young seedling stages than at germination. The plants that were transplanted to the potometers continued to grow in concentrations at which there was practically no germination. All sodium carbonate treatments maintained 100 per cent growth for 20 days, but in the highest concentration of 0.35 per cent, death occurred in 2 months. Chlorides maintained a fair growth up to 0.15 per cent but were killed by 0.35 per cent. Sulfates in the highest concentrations used did not kill the transplanted seedlings.

In the 2- and 3-salt combinations the salts maintain their own toxicity factor quite consistently. In the 3-salt combinations where sulfates or chlorides predominate, the toxic effects are not entirely additive, but appear to increase faster than would seem warranted from the effects of the single salts. In view of the fact that the salts usually appear in combinations in the field, this is especially important in obtaining a stand of alfalfa. It is possible that where the osmotic pressure already approaches the maximum for plant growth, the addition of a small amount of salt produces a greater effect on the plant than if the osmotic pressure were less.

It is especially true in the 3-salt combinations that the plants failed to develop strong crowns, and that many of the plants having 3 to 8 culms died

even after 3 or 4 months of established growth. A comparison of the number of plants alive 5 months after planting shows that a larger percentage persisted in salt concentrations near the toxic limit for alfalfa, when planted as seedlings, than when they were grown from seed. Obviously in the highest concentrations of carbonates and chlorides, or combinations where these salts predominate, the transplanted seedlings were also killed. Much of the decrease in yield in the last 24 potometers is due to a low number of growing plants.

In seeding alfalfa, the fact that mature plants withstand a concentration of salts materially higher than that at which the seed will germinate, can well be made use of by planting the seed at a time when the salts have been washed down, and by keeping them washed down by careful irrigation until the young plants are well established. In small areas when alfalfa will grow if a stand is secured it might even be practical to transplant seedlings from a good area. This is one method of securing a uniform stand on alkali spots so prevalent in alfalfa fields of the arid sections.

#### THE EFFECT OF ALKALI SALTS ON THE YIELD OF ALFALFA

In discussing the effect of alkali salts on crop growth, the crop yields were divided into 2 groups. This was done in order to allow a uniform number of plants to develop in each treatment. The fourth and fifth cuttings, therefore, represent more nearly the actual effect of alkali salt concentrations on alfalfa as would be apparent under field conditions. It is well known that the greatest effect of alkali salt is exerted on the germination, the rate of germination and the growth of young plants.

A consideration of the effect of sodium carbonate on yield of alfalfa, shows that alfalfa is able to produce normal yields even when the added concentration of salt is 0.6 per cent, with a recovery of 0.2 per cent. When the recoverable salt concentration is above 0.2 per cent there is a total lack of growth. It is notable that up to 0.15 per cent recoverable salt concentrations, marked stimulation occurs on the growth of alfalfa, the growth increasing in proportion to the recoverable salts present until the concentration of 0.15 per cent is reached. This stimulation is especially noticed in the first cutting of alfalfa and continues in a slightly decreasing degree throughout the entire 5 cuttings.

Sodium chloride treatments show a depressing effect on yield even in the smallest concentrations. Additions of 0.2 per cent salt cuts the yield approximately one-half, while 0.4 per cent greatly inhibits growth. The greatest effect of sodium chloride additions on yield is noted during the early stages of growth. At this stage alfalfa appears to be more sensitive to chlorides. Young plants that survive the chloride additions appear to become more resistant as time goes on. The fourth and fifth cuttings showed a slight stimulation in growth in the 0.1 per cent added salt. This same concentration showed a reduced yield for the first 3 cuttings.

Sodium sulfate treatments all showed normal growth of alfalfa for all concentrations in the first cuttings. The fourth and fifth cuttings showed a slight stimulation in the lower concentrations. The highest sulfate concentration, 0.9 per cent, was too low to show any marked effect on yield which indicates that alfalfa is quite resistant to sodium sulfate.

In sodium carbonate and sodium chloride combinations where yields are decreased, the major effect should be attributed to the sodium chloride additions even when sodium chloride constitutes only a small part of the added salts. This same conclusion is drawn when sodium chloride is found in combination with sodium sulfate. It is immaterial whether the sulfate additions are high or low within the limits of this experiment, for whenever even small amounts of sodium chloride are present in combination the major effect of decreasing yield must be attributed chiefly to the sodium chloride.

The sodium carbonate and sodium sulfate combinations, each of which shows unusual growth in many of the concentrations, show similar effects when the total salt present in the combination does not exceed the tolerance limit of the predominating salt. Raising the total salt concentration by addition of the minor salt immediately shows its effect by reduced yields.

Small amounts of sodium chloride show an effect in reducing yield in all the triple salt combinations. The greatest effect is always noted, even with these small sodium chloride additions, when the sum of the other two salts, sodium carbonate and sodium sulfate, is very near the maximum tolerance concentration for alfalfa. Under these conditions the plants seem to be very sensitive to small additions of sodium chloride, since duplicate treatments may differ from almost no growth to nearly normal growth, depending undoubtedly upon slight difference in the physical condition of the soil or the equilibrium in the soil solution. The yields are materially reduced in all 3-salt combinations when the concentration of total salts is high.

#### THE EFFECT OF ALKALI SALTS ON THE GROWTH OF CORN AND SWEET CLOVER

After the 5 cuttings of alfalfa had been removed, the potometers were allowed to remain exposed to the fall and winter rains. Considerable leaching of the alkali salts took place, either by soil percolation or by water overflowing the potometers. The first 24 potometers were not water tight, hence considerable leaching of the soils took place by percolation. In the heavy carbonate applications the soil had developed such a compact physical structure that water percolated with extreme slowness and in these instances the salts that were removed were mainly washed from the top of the potometers by overflow water.

This series of potometers offered an excellent opportunity to study the effect of leaching as it would occur in alkali soil during exposure to rains or flooding by irrigation. It also offered an opportunity to study the effect of these leached alkali soil combinations on 2 additional crops, corn and sweet clover. The following summer the soil was prepared and 10 kernels



of Reed's yellow dent corn and 25 seeds of biennial, white sweet clover were planted together in each potometer. This clover seed was unscarified, hence germination took place slowly. The data on germination, therefore, have little value as far as drawing conclusions as to the effect of alkali salts. A close inspection of the data indicates that in a few cases the number of plants became the limiting factor in the total yield, since the entire number of sweet clover seeds that germinated were allowed to grow. The corn, however, was thinned to 3 stalks per potometer. Table 2 contains the original treatments of the potometer and final sampling after the crops were grown, together with the germination and crop data for these crops.

Corn, with its large seed and strong sprout, germinates well even in high concentration of alkali. The only concentration that inhibited germination was a recoverable concentration of 0.26 per cent or more of sodium carbonate. In its later growth, corn is quite sensitive to all salts; carbonates in concentrations of 0.12 per cent produced marked decrease and 0.18 per cent usually killed the plants. In combination with a small percentage of chlorides, 0.15 per cent recovery was enough totally to destroy growth. Any concentration above 0.1 per cent reduced the yield below 50 per cent of the check when in combination with other salts, and nearly as much when present alone in the soil.

In the treatments consisting entirely of sodium chloride, leaching throughout the fall and winter months removed the greater part of the chlorides. Crop yields were, however, very poor in spite of the low recovery of sodium chloride salts. The maximum found in these soils was 0.06 per cent sodium carbonate, which was largely formed in the soil as a direct result of the leaching of chloride ion. This has been conclusively shown by Cummings and Kelly (1) to occur when chlorides are leached from soil. In all the combinations where sodium chloride was originally present and exposed to the leaching action, there is a decrease in crop yield that can be attributed directly to the influence of the newly formed sodium carbonate, induced by leaching out of the chloride ion. This action persists whenever large quantities of added chlorides have been removed from the soil through leaching.

Sulfates are less harmful than carbonates or chlorides, but in the higher recoveries of 0.57 per cent, produced very little growth of corn. With a recovery of 0.23 per cent, the yield is cut approximately one-half. As is true with the chloride treatment, leaching removes much of the sodium sulfate.

Sweet clover presents a situation that is largely different from the other crops. The germination data vary widely, and show no definite relation to the salt content of the soil. This is no doubt due in a large measure to the type of unscarified seed used. Concentration of carbonates equalling or exceeding 0.25 per cent recoverable salts inhibited germination in all cases. All plants that germinated were allowed to grow. It is apparent, however, that the total yield of dry matter is far more dependent on the condition of

TABLE 2  
Corn and sweet clover tolerance

NUM- BER	TREATMENT			SALT RECOVERY AFTER HARVESTING				CROP GROWTH			
	Na <sub>2</sub> CO <sub>3</sub>	NaCl	Na <sub>2</sub> SO <sub>4</sub>	Na <sub>2</sub> CO <sub>3</sub>	Total equiva- lent Na <sub>2</sub> CO <sub>3</sub>	NaCl	Na <sub>2</sub> SO <sub>4</sub>	Corn		Sweet clover	
	per cent	per cent	per cent	per cent	per cent	per cent	per cent	Number of plants	Yield	Number of plants	Yield
1	Check			0.001	0.031	0.000	0.007	10	100.0	10	100
3	0.20			0.036	0.083	0.000	0.007	5	80.1	6	145
5	0.40			0.073	0.123	0.000	0.005	12	87.1	7	185
7	0.60			0.088	0.180	0.001	0.005	9	29.9	5	187
9	0.90			0.119	0.339	0.001	0.005	0	0.0	0	0
11		0.10		0.005	0.044	0.002	0.003	12	98.3	7	65
13		0.20		0.012	0.053	0.000	0.004	8	87.8	3	117
15		0.40		0.013	0.060	0.000	0.005	12	45.1	16	457
17			0.20	0.000	0.038	0.000	0.035	11	83.7	12	132
19			0.40	0.001	0.033	0.000	0.106	9	73.1	12	107
21			0.60	0.001	0.031	0.000	0.230	8	52.9	15	270
23			0.90	0.000	0.028	0.000	0.411	9	45.7	8	130
25	0.10	0.10		0.013	0.060	0.000	0.007	10	71.4	10	187
27	0.30	0.05		0.043	0.115	0.038	0.006	13	62.6	7	305
29	0.10	0.30		0.014	0.059	0.118	0.011	17	20.2	8	207
31	0.60	0.10		0.112	0.148	0.082	0.009	11	3.7	4	50
33	0.20	0.20		0.030	0.075	0.089	0.008	17	56.0	8	197
35		0.05	0.20	0.005	0.036	0.013	0.076	16	73.9	14	137
37		0.30	0.10	0.005	0.046	0.078	0.052	15	54.9	10	290
39		0.10	0.40	0.000	0.035	0.048	0.225	12	59.0	12	100
41		0.10	0.60	0.000	0.025	0.035	0.381	16	88.6	7	200
43	0.10		0.10	0.007	0.045	0.000	0.051	18	97.0	11	182
45	0.20		0.20	0.021	0.070	0.000	0.085	17	83.2	7	185
47	0.30		0.40	0.043	0.094	0.000	0.079	13	79.1	9	240
49	0.20		0.60	0.003	0.054	0.000	0.290	15	68.0	4	182
51	0.10		0.10	0.129	0.201	0.000	0.044	9	20.0	4	37
53	1.00		0.10	0.194	0.272	0.001	0.054	0	0.0	0	0
55	0.05	0.05	0.05	0.002	0.040	0.000	0.045	17	88.1	14	227
57	0.10	0.10	0.10	0.015	0.058	0.008	0.048	7	70.7	9	80
59	0.20	0.10	0.10	0.026	0.075	0.048	0.059	18	69.3	11	310
61	0.40	0.05	0.10	0.069	0.167	0.039	0.068	18	38.0	14	495
67	0.20	0.05	0.40	0.018	0.061	0.017	0.188	15	33.3	5	35
69	0.20	0.05	0.80	0.010	0.048	0.033	0.572	12	18.5	7	212
71	0.05	0.05	0.60	0.001	0.030	0.001	0.303	14	35.5	9	95
73	1.00	0.05	0.10	0.206	0.267	0.029	0.058	0	0.0	0	0
77	0.30	0.20	0.20	0.048	0.103	0.003	0.030	17	30.3	10	38
79	0.10	0.20	0.20	0.075	0.052	0.002	0.107	13	61.1	10	112
81	0.10	0.40	0.10	0.052	0.068	0.015	0.031	17	30.8	14	280

growth than on the number of plants. Sodium carbonate shows persistent toxicity at germination whenever 0.1 per cent of recoverable sodium carbonate is found. Concentrations of induced carbonates (that is carbonates

found in soils from which sodium chloride is leached) also show toxic effects on germination, even though present in amounts less than 0.1 per cent recoverable salt.

Whenever germination takes place in the sodium carbonate treatments, the sweet clover yields are higher than the check. Carbonates appear to stimulate the growth of sweet clover, if the seed germinates and the plant secures a start. This stimulation persists with other salt combinations and its effect predominates over the other salts. Generally speaking the stimulation varies in the same direction as the carbonate content.

Sodium chloride was not present in amounts large enough to influence crop growth. Where heavy applications had originally been made, subsequently followed by leaching, there was found some stimulation of growth which might be attributed to the effect of the induced or newly formed sodium carbonate in the soil. In these cases the actual amount of chloride present in the soil is insignificant.

Sodium sulfate was leached out to some extent, but high concentration still remained in the soil. While there was no material toxicity evident from the effect of sulfates, it is worthy of note that the stimulation in growth where sulfates predominate is less than for carbonates.

Attention is called to the effect of leaching on the salt content of the potometers as shown by analyses made after the growth of the corn and sweet clover. Only a small amount of the carbonates was removed from the soil by leaching. The chlorides were almost entirely leached out when present alone or with the sulfates. In combinations with sodium carbonate there was a decided reduction in leaching of both of the other 2 salts. This is undoubtedly due to a protective influence of the carbonates. That is, the direct effect of carbonate salts on the physical condition of the soil prevented in a large measure the removal of sodium chloride and sodium sulfate salts by leaching.

#### SUMMARY

1. Five crops of alfalfa were grown in potometers containing artificial alkali soil made by additions of sodium carbonate, sodium chloride and sodium sulfate, singly and in varying combinations.
2. The maximum tolerance of alfalfa for sodium carbonate when grown on Boise silt loam soil closely approximates 0.6 per cent added salt or 0.2 per cent recoverable sodium carbonate.
3. The amount of sodium chloride which permits a normal yield of alfalfa for the fourth and fifth cuttings is 0.2 per cent added salt and 0.16 per cent recoverable salt. This concentration materially reduces the yield of the first 3 crops.
4. The highest addition of sodium sulfate, 0.9 per cent with a recovery of 0.74 per cent was not great enough to materially affect the yield.
5. All concentrations of added sodium carbonate salts which yield re-

coverable salts up to 0.15 per cent show marked stimulation of growth of alfalfa.

6. Sodium sulfate additions which show recoverable salts up to 0.37 per cent stimulate the growth of alfalfa.

7. In the 2- or 3-salt combinations each salt maintains its characteristic influence when in predominance, and shows additive toxicity when the salts are present in similar amounts. Small amounts of chlorides are especially toxic in combination with the other 2 salts.

8. The effect of the alkali salts on the germination of alfalfa is greater than on the plants when they have established growth. Of the 3 salts, sodium chloride shows the greatest toxic effect on germination, with sodium carbonate and sodium sulfate following in the order named.

9. After the alfalfa was harvested the soils were leached by rain; a crop of corn and sweet clover was grown on these soils the following season.

10. These studies show corn to be very sensitive to all alkali salts, especially sodium carbonate.

11. The outstanding, results of this fragmentary investigation on sweet clover show that sweet clover will withstand the effect of large amounts of carbonates in the soil and will also overcome unfavorable physical conditions whether produced by added carbonates, or by leaching other salts from the soil.

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THE TERNARY SYSTEMS  $\text{CaO-Fe}_2\text{O}_3\text{-CaSO}_4$  AND  $\text{CaO-Al}_2\text{O}_3\text{-CaSO}_4$   
AS EXPLAINING THE RETENTION OF SULFATES BY  
HEAVILY LIMED SOIL

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In a preliminary paper (6), covering a 2-year period, it was shown that *excessive* additions of  $\text{CaO}$  practically inhibited an outgo of sulfates in lysimeter leachings. A later 8-year-period report (7) demonstrated that the initial depressive effect was not permanent. Comparisons between leaching and rainfall data showed that, for a time, the heavily limed soils also retained a large part of the sulfates which were brought down by rain waters. The retentive properties of the subsoil were still more marked. The relationships between the continued causticity and sulfate content of leachings were given special consideration (7, p. 19-22).

In another project sulfate outgo from applications of  $\text{CaSO}_4$ , pyrite, and elementary sulfur was studied over a 5-year period (8). That contribution showed that *heavy* liming initially depressed sulfate leachings from all three forms of sulfur, and that the intensive initial depression persisted only in the case of the pyrite.

Giving due regard to inhibition of sulfonation by the heavy lime treatments during the persistence of causticity and to the depressed solubility of  $\text{CaSO}_4$  in aqueous solutions of  $\text{Ca(OH)}_2$ , as reported upon (7, 8) the greatly depressed outgo of sulfates must have been due in the main to either one or both of two causes—desulfonation or absorption. If absorption were the explanation, then arises the possibility of this being caused by either the granulated soil or the bulky lime treatment, *per se*.

Further attack was made by means of aqueous suspensions of  $\text{Ca(OH)}_2$ , alone and with soil in short-time laboratory investigations (9). In this work the previously observed phenomenon of sulfate retention by heavily limed soil was duplicated. The absorption of the sulfate radical effected by the soil suspensions in water solutions of  $\text{Ca(OH)}_2$  was almost immediate and absolute, and it prevailed during the maintenance of the  $\text{Ca(OH)}_2$  in the solution phase. However, upon reversion of hydrate to carbonate by passage of  $\text{CO}_2$ , or by addition of soluble carbonates, the sulfate absorption was almost immediately nullified. Though equivalent to only a fraction of that found in the soil-lime suspensions, a similar retention with subsequent liberation was also obtained in aqueous suspensions of the high-grade commercial hydrate in the absence of soil.

In these laboratory studies, the possibility of de-sulfonation was eliminated, for the intensity of the alkalinity and the brevity of the experimental periods were such as to preclude biological activities. With elimination of biological factors, it was evident that the removal of sulfates from solution was due either to adsorption, or to the formation of insoluble sulfate complexes. The latter possibility was pointed out in the immediately preceding contribution (9, p. 77).

Soil organic matter was next eliminated as a factor by using suspensions of thoroughly ignited soils. These ignited residues were found to have fixing power even greater than that of the unignited soils. The problem then narrowed to a consideration of mineral components. Since silica, iron and alumina were the preponderant components of the more active ignited residues, the indefinite soil mass was discarded in favor of these three substances. These questions then arose:

- (a) Are  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$  or  $\text{Al}_2\text{O}_3$  responsible either singly or jointly for the  $\text{CaSO}_4$  absorptions from aqueous  $\text{Ca}(\text{OH})_2$ - $\text{CaSO}_4$  solutions?
- (b) Are the absorptions of sulfates attributable to physical or chemical phenomena?
- (c) If of the chemical nature, what are the compositions and characteristics of intermediate and final products?

EXPERIMENT 1. ABSORPTIONS OF  $\text{CaSO}_4$  BY DIFFERENT  $\text{SiO}_2$  AND  $\text{Fe}_2\text{O}_3$  COMBINATIONS, AS INFLUENCED BY  $\text{Ca}(\text{OH})_2$

Three solids, ground quartz, precipitated silicic acid and finely ground dried hydrated  $\text{Fe}_2\text{O}_3$ , were used in addition to  $\text{Ca}(\text{OH})_2$  in the first  $\text{Ca}(\text{OH})_2$ - $\text{CaSO}_4$  absorption experiment. The silicic acid was a purchased material.

The dried hydrated ferric oxide was prepared in the laboratory from an ammoniacal precipitate. After thorough washing, the precipitate was dried in a water oven, pulverized and passed through a 120-mesh sieve. Its  $\text{Fe}_2\text{O}_3$  content was found to be 84.82 per cent. The amounts of both  $\text{Ca}(\text{OH})_2$  and  $\text{CaSO}_4$  absorbed by the solids from aqueous solution were determined by analyses of aliquots of the clear supernatant solutions before and after contact periods.

As previously stated, increase in charges of a high-grade commercial lime gave increased sulfate absorption from a calcium sulfate solution. But, in spite of the small percentage of impurities, the aggregate of such reached considerable proportions in the larger lime charges. It was not established, therefore, whether the absorption of  $\text{CaSO}_4$  was due to the mass of calcium hydrate, *per se*, or to its impurity content. In the present work that uncertainty was provided against by the use of  $\text{CaO}$  derived from electrically ignited "C. P." precipitated  $\text{CaCO}_3$ .

Silica in both forms was used in a constant amount, 125 gm. Eighty per cent of the quartz passed through a 100-mesh sieve, while the precipitated silicic acid was largely colloidal. The ground quartz contained traces of iron and sulfates. The precipitated silica also carried soluble sulfates.



The dry materials were weighed into 500-cc. Erlenmeyer flasks. A constant of 400 cc. of a nearly saturated aqueous solution of  $\text{CaSO}_4$  was introduced and the flasks tightly corked. The contents were agitated for one minute at one-hour intervals during the first 2 working days and twice daily for the next 14 days. Aliquots of 50 cc. were withdrawn for titrations and sulfate determinations at the end of these two periods. Filtration of aliquots was necessary only in the combinations containing silicic acid without lime.

TABLE 1

*CaSO<sub>4</sub> absorption by aqueous suspensions of dried hydrated ferric oxide, alone and with ground quartz, with and without Ca(OH)<sub>2</sub>*

SOLIDS SUSPENDED IN 400 CC.			DATA DERIVED FROM 50 CC. ALIQUOTS				TOTALS AS BaSO <sub>4</sub>		
Other than lime		Weight of Ca(OH) <sub>2</sub>	Titration against 0.5 N acid		BaSO <sub>4</sub> precipitate		Unab- sorbed after 16 days	Ab- sorbed after 16 days	
Material	Weight of Fe <sub>2</sub> O <sub>3</sub>		After 48 hours	After 16 days	After 48 hours	After 16 days			
	gm.	gm.	cc.	cc.	gm.	gm.	gm.	gm.	
Series A	None.....	None	...	...	0.1708	0.1708	1.3664	...	
	None.....	1	4.1	4.1	0.1641	0.1685	1.3436	0.0228	
	None.....	6	4.1	4.1	0.1685	0.1646	1.3207	0.0357	
	Hydrated Fe <sub>2</sub> O <sub>3</sub> .....	0.4	None	0	0	0.1661	0.1668	1.3337	0.0327
		0.4	1	4.1	4.1	0.1585	0.1470	1.1875	0.1789
		0.8	None	0	0	0.1633	0.1628	1.3029	0.0635
		0.8	1	4.1	4.1	0.1484	0.1268	1.0360	0.3304
		1.6	None	0	0	0.1615	0.1436	1.1667	0.1997
		1.6	1	4.1	4.1	0.1307	0.1030	0.8517	0.5147
	Quartz alone.....	None	0	0	0.1681	0.1681	1.3448	...	
		1	4.1	4.1	0.1667	0.1706	0.3609	0.0161	
		6	4.1	4.1	0.1638	0.1565	1.2593	0.0855	
		0.4	None	0	0	0.1670	0.1670	1.3360	0.0088
		0.4	1	4.1	4.1	0.1586	0.1392	1.1330	0.2118
		0.8	None	0	0	0.1666	0.1647	1.3195	0.0253
		0.8	1	4.1	4.1	0.1486	0.1180	0.9746	0.3702
		1.6	None	0	0	0.1624	0.1615	1.2929	0.0519
		1.6	1	4.1	4.1	0.1285	0.0840	0.7165	0.6283
Series B	Quartz.....	None	0	0	0.1681	0.1681	1.3448	...	
		1	4.1	4.1	0.1667	0.1706	0.3609	0.0161	
		6	4.1	4.1	0.1638	0.1565	1.2593	0.0855	
	Quartz and Fe <sub>2</sub> O <sub>3</sub> .....	0.4	None	0	0	0.1670	0.1670	1.3360	0.0088
		0.4	1	4.1	4.1	0.1586	0.1392	1.1330	0.2118
		0.8	None	0	0	0.1666	0.1647	1.3195	0.0253
		0.8	1	4.1	4.1	0.1486	0.1180	0.9746	0.3702
		1.6	None	0	0	0.1624	0.1615	1.2929	0.0519
		1.6	1	4.1	4.1	0.1285	0.0840	0.7165	0.6283

In those cases colloidal silica was readily removed by filtration through a Büchner, after the addition of a very small amount of colloidal ferric oxide. Appreciable absorption was found, and is reported quantitatively, only where Fe<sub>2</sub>O<sub>3</sub> was added. In table 2 the final results are given in condensed form, both in gm. and in per cent.

Silica, both colloidal and crystalloidal, was found to be inactive in the removal of calcium sulfate from aqueous Ca(OH)<sub>2</sub> solutions. The former was quickly precipitated as calcium silicate, with complete elimination of

$\text{Ca(OH)}_2$ , even in the 6-gm. charge; while the latter was practically inert. The small absorption indicated in both  $\text{CaO-SiO}_2$  suspensions can hardly be attributed to the pulverulent calcium silicate, since the amount absorbed by the 6-gm. charge of  $\text{CaO}$  plus silica was even less than that from the 1-gm. charge.

The "C. P." lime acted differently from the high-grade commercial product previously studied. No appreciable absorption was caused by the solid-phase excess of pure lime and no proportionate increase resulted from the increase in surface, or period of contact, in the larger charges of the C. "P". material. With the  $\text{CaSO}_4$  concentration used no appreciable "common ion effect" was in evidence. That is, the concentration of the aqueous solu-

TABLE 2

*Calcium sulfate absorption by the solids  $\text{Fe}_2\text{O}_3$  and quartz, singly and in combinations, with and without excesses of calcium hydrate in aqueous suspensions*

SOLID MATERIALS	AMOUNT OF		CaSO <sub>4</sub> REMOVED FROM SOLUTION			
			Actual amount*		Fraction of total originally in solution	
	Fe <sub>2</sub> O <sub>3</sub>	CaO	Series A no silica	Series B quartz	Series A no silica	Series B quartz
	gm.	gm.	gm.	gm.	per cent	per cent
CaO only.....	...	1	0.0133	0.0094	1.7	1.2
	...	6	0.0208	0.0593	2.6	6.3
Hydrated Fe <sub>2</sub> O <sub>3</sub> .....	0.4	..	0.0191	0.0051	2.4	0.7
	0.8	..	0.0370	0.0148	4.7	1.9
	1.6	..	0.1165	0.0303	14.6	3.9
Hydrated Fe <sub>2</sub> O <sub>3</sub> and CaO.....	0.4	1	0.1041	0.1235	13.1	15.8
	0.8	1	0.1927	0.2159	24.2	27.5
	1.6	1	0.3002	0.3664	37.7	46.7

\* Solution-constant plus impurities of solids give total  $\text{CaSO}_4$  occurrences of: 0.7969 gm., Series A; 0.7843 gm., Series B.

tion of  $\text{CaSO}_4$  was practically the same as that of the saturated  $\text{Ca(OH)}_2$  solution after 16 days. From the foregoing it is evident that the previously observed absorption of sulfate (9, p. 66) by the high-grade commercial product was not due to the quantity of hydrate, but rather to its impurities.

As compared with the combinations which included  $\text{Ca(OH)}_2$ , the unsupplemented hydrated  $\text{Fe}_2\text{O}_3$  charges (table 1) show slight effect upon the concentration of  $\text{CaSO}_4$ . The slight sulfate fixation by the  $\text{Fe}_2\text{O}_3$ , in the absence of lime, may be ascribed to adsorption, as has been pointed out by Lichtenwalner, Flenner and Gordon (6).

In the hydrated  $\text{Fe}_2\text{O}_3$ -CaO groups it is evident that the lime has greatly activated the added ferric oxide. If this phenomenon was caused by chemical reaction between the ferric oxide and sulfate and lime, the resultant com-

pound is one as yet not described. The decided and progressive loss of characteristic color of the hydrated  $\text{Fe}_2\text{O}_3$  suspension and the continued absorption of sulfate indicate chemical reaction, rather than adsorption. This indication will be amplified and clarified in the following pages. In comparisons between the  $\text{Fe}_2\text{O}_3$ -CaO and  $\text{Fe}_2\text{O}_3$ -CaO-quartz combinations some increase in absorption occurred when the relatively inert quartz was present. The flasks were frequently agitated and the readily observable abrasive action of the quartz upon the ferric oxide was reflected in the greater reactivity of the powdered prepared hydrated oxide.

These points are brought out by the analyses of experiment 1. (a) Colloidal silica and its lime-reaction product may be disregarded as factors responsible for any appreciable absorption of sulfates which follows excessive  $\text{Ca}(\text{OH})_2$  treatments. (b) Colloidal silica in excess eliminates  $\text{Ca}(\text{OH})_2$ , through the immediate formation of calcium silicate, thereby precluding appreciable  $\text{CaSO}_4$  absorption. (c) When supplemented by  $\text{Ca}(\text{OH})_2$ , ferric oxide exerts a remarkably absorptive capacity for  $\text{CaSO}_4$ .

EXPERIMENT 2. ABSORPTIONS OF  $\text{CaSO}_4$  BY FRESHLY PRECIPITATED HYDRATED OXIDES OF IRON AND ALUMINIUM, AS INFLUENCED BY  $\text{Ca}(\text{OH})_2$

The second experiment embraces comparisons between the absorptive properties of *freshly precipitated* hydrated oxides of iron and aluminium. This experiment was begun before the completion of experiment 1. The first study had advanced to a point where it had been determined that the CaO- $\text{Fe}_2\text{O}_3$  combinations absorbed large amounts of  $\text{CaSO}_4$ . It was thought possible that the undried fresh precipitate might prove more reactive than the dried product. The hydrated  $\text{Fe}_2\text{O}_3$  used in experiment 2 was, therefore, introduced as a wet precipitate. It was obtained from the oven-dried hydrated product by solution and re-precipitation. A mass of material more than sufficient for all of the proposed combinations was thoroughly washed and the gel protected against change during moisture determinations. Moist charges were weighed into the several flasks. This procedure eliminated the factors of compacting the gel and its adhesion to the filter.

Mention has been made of the abrasive action of the quartz during agitation of the sifted, dried hydrated  $\text{Fe}_2\text{O}_3$ . Ground quartz was accordingly used also with the two freshly precipitated hydrated oxides.

The hydrated oxide of aluminium was made by dissolving metallic aluminium in sodium hydroxide and neutralizing the excess of hydrate with hydrochloric acid. The wet precipitate was washed nearly free of chlorides. Its moisture content was determined by ignition and the moist charges were weighed into 500-cc. flasks, as in the case of the hydrated ferric oxide. Both oxides were used in quantities which gave 2, 4 and 8 milli-mols. A 1-gm. charge of the same CaO and the same volume and concentration of  $\text{CaSO}_4$  were used, as in experiment 1. Analytical manipulations were identical with those followed in the first experiment.

The titration values, barium sulfate determinations and calcium sulfate absorptions are given in tables 3 and 4. Further comparisons are also made in table 5, which carries calculations of the molecular proportions involved in the several reactions.

Confirming the findings of experiment 1, the data of table 3 show a parallel between combinations 1, 2 and 3—sulfate solution and freshly precipitated  $\text{Fe}_2\text{O}_3$  alone—and combinations 7, 8 and 9, embodying sulfate solution, freshly

TABLE 3

*Absorption of  $\text{CaSO}_4$  by freshly precipitated hydrated  $\text{Fe}_2\text{O}_3$  as affected by a constant supplement of  $\text{CaO}$ ,\* with and without quartz†*

COMBINATION NUMBER	SOLIDS SUSPENDED IN 400 CC. AQUEOUS SOLUTION OF $\text{CaSO}_4$ ‡	MILLI-MOLS OF $\text{Fe}_2\text{O}_3$	DATA DERIVED FROM 50 CC. ALIQUOTS				TOTAL ABSORPTIONS AT END OF 16 DAYS	
			Titrations against 0.5 N acid		$\text{BaSO}_4 \rightleftharpoons \text{CaSO}_4$			
			After 48 hours	After 16 days	After 48 hours	After 16 days	CaO	$\text{CaSO}_4$
			cc.	cc.	gm.	gm.	gm.	gm.
1	$\text{Fe}_2\text{O}_3$ alone.....	2	0	0	0.1690§	0.1765§	.....	0.0064
2	$\text{Fe}_2\text{O}_3$ alone.....	4	0	0	0.1662	0.1623	.....	0.0532
3	$\text{Fe}_2\text{O}_3$ alone.....	8	0	0	0.1486	0.1466	.....	0.1278
4	$\text{Fe}_2\text{O}_3$ and $\text{CaO}$ .....	2	4.1	4.1	0.1040	0.0755		0.4440
5	$\text{Fe}_2\text{O}_3$ and $\text{CaO}$ .....	4	4.1	2.9	0.0820	0.0266	0.6180	0.6563
6	$\text{Fe}_2\text{O}_3$ and $\text{CaO}$ .....	8	2.8	1.8	0.0555	0.0268	0.8840	0.6710
7	$\text{Fe}_2\text{O}_3$ and quartz.....	2	0	0	0.1678	0.1658	.....	0.0383
8	$\text{Fe}_2\text{O}_3$ and quartz.....	4	0	0	0.1633	0.1664	.....	0.0384
9	$\text{Fe}_2\text{O}_3$ and quartz.....	8	0	0	0.1452	0.1470	.....	0.1281
10	$\text{Fe}_2\text{O}_3$ , $\text{CaO}$ and quartz.....	2	4.1	4.1	0.1003	0.0598		0.5102
11	$\text{Fe}_2\text{O}_3$ , $\text{CaO}$ and quartz.....	4	3.8	2.7	0.0735	0.0342	0.6820	0.6303
12	$\text{Fe}_2\text{O}_3$ , $\text{CaO}$ and quartz.....	8	3.0	2.1	0.0407	0.0246	0.7520	0.6886

\* 1.0 gm. equivalent to 17.8 milli-mols.

† 125 gm.

‡ 0.8127 gm. equivalent to 5.97 milli-mols.

§  $\text{CaSO}_4$  solution gave 0.1708-gm.  $\text{BaSO}_4$  equivalent.

|| Solid phase  $\text{Ca}(\text{OH})_2$  present.

precipitated  $\text{Fe}_2\text{O}_3$  and quartz. Fairly close agreement was also found between calcium sulfate absorptions by  $\text{CaO-Fe}_2\text{O}_3$  and  $\text{CaO-Fe}_2\text{O}_3$ -quartz combinations. Similar observations resulted from the  $\text{Al}_2\text{O}_3$  parallels of table 4. These two gels were so dispersed as to minimize abrasive action during agitation with the quartz.

Only relatively small amounts  $\text{CaSO}_4$  were absorbed by the freshly precipitated hydrated  $\text{Fe}_2\text{O}_3$  alone. However, appreciable differences were indicated as to amounts absorbed by the 2 milli-mol and 8 milli-mol charges.

It also appears that the absorption evidenced after 48 hours was equal to that found at the end of 16 days. The same statements hold true for precipitated hydrated  $\text{Al}_2\text{O}_3$  alone, as will be seen by reference to table 4.

Since the general principles shown by the three  $\text{CaO-Fe}_2\text{O}_3$  combinations 4, 5 and 6 of table 3 also obtain for combination 10, 11 and 12, these two sets may be considered as duplicates. The same may be said of the corresponding  $\text{CaO-Al}_2\text{O}_3$  combinations in table 4. The principal difference between

TABLE 4  
*Absorption of  $\text{CaSO}_4$  by freshly precipitated hydrated  $\text{Al}_2\text{O}_3$  as affected by a constant supplement of  $\text{CaO}$ ,\* with and without quartz†*

COMBINATION NUMBER	SOLIDS SUSPENDED IN 400 CC. AQUEOUS SOLUTION OF $\text{CaSO}_4$ ‡	MILLI-MOLS OF $\text{Al}_2\text{O}_3$	DATA DERIVED FROM 50 CC. ALIQUOTS				TOTAL ABSORPTION AT END OF 16 DAYS	
			Titrations against 0.5 N acid		$\text{BaSO}_4 \rightleftharpoons \text{CaSO}_4$		CaO	$\text{CaSO}_4$
			After 48 hours	After 16 days	After 48 hours	After 16 days		
1	$\text{Al}_2\text{O}_3$ alone .....	2	0	0	0.1795§	0.1690§	....	0.0184
2	$\text{Al}_2\text{O}_3$ alone .....	4	0	0	0.1617	0.1591	....	0.0691
3	$\text{Al}_2\text{O}_3$ alone .....	8	0	0	0.1475	(lost)	....	0.1248
4	$\text{Al}_2\text{O}_3$ and CaO .....	2	4.1	4.1	0.0657	0.0182		0.7001
5	$\text{Al}_2\text{O}_3$ and CaO .....	4	3.1	2.7	0.0025	0.0024	0.6920	0.8014
6	$\text{Al}_2\text{O}_3$ and CaO .....	8	1.1	1.1	0.0005	0	0.8770	0.8124
7	$\text{Al}_2\text{O}_3$ and quartz .....	2	0	0	0.1700	0.1716	....	0.0133
8	$\text{Al}_2\text{O}_3$ and quartz .....	4	0	0	0.1530	0.1644	....	0.0526
9	$\text{Al}_2\text{O}_3$ and quartz .....	8	0	0	0.1478	0.1480	....	0.1226
10	$\text{Al}_2\text{O}_3$ , CaO and quartz .....	2	4.1	4.1	0.0457	0.0062		0.7608
11	$\text{Al}_2\text{O}_3$ , CaO and quartz .....	4	3.4	2.7	0.0015	0.0024	0.6880	0.8020
12	$\text{Al}_2\text{O}_3$ , CaO and quartz .....	8	1.1	1.1	0.0002	0	0.8770	0.8126

\* 1.0 gm. equivalent to 17.8 milli-mols.

† 125 gm.

‡ 0.8127 gm. equivalent to 5.97 millimols.

§  $\text{CaSO}_4$  solution gave 0.1708 gm.  $\text{BaSO}_4$  equivalent.

|| Solid phase  $\text{Ca(OH)}_2$  present.

the  $\text{Fe}_2\text{O}_3$  data of table 3 and the  $\text{Al}_2\text{O}_3$  data of table 4 is that of the speed of absorption of both  $\text{Ca(OH)}_2$  and  $\text{CaSO}_4$ . A considerable absorption of sulfate took place between the end of the initial period of 48 hours and the 16-day period in the six  $\text{Fe}_2\text{O}_3$  treatments. However, practically all of the sulfate had been absorbed in the  $\text{Al}_2\text{O}_3$  combinations at the end of the first contact period of 48 hours, for both the 4- and 8-milli-mol charges.

If we assume that the slight calcium sulfate absorption by the unsupplemented oxides of iron and aluminium is a physical phenomenon, the equi-

libria attained in combinations 1, 2, 3 and 7, 8, 9 are those which would be expected. On the other hand, the augmented and continued absorption brought about by the supplementary  $\text{Ca(OH)}_2$ , combinations 4, 5 and 6, and 10, 11 and 12 is more characteristic of a chemical phenomenon.

From the titration values, it is evident that large and roughly proportionate amounts of  $\text{Ca(OH)}_2$  were absorbed by both of the hydrated oxides; but the minimum charges of 2 milli-mols did not absorb sufficient lime to prevent the maintenance of a saturated solution. On the other hand, the 4- and 8-milli-mol charges of both oxides continued to combine with such a large

TABLE 5  
*Molecular proportion comparisons of total  $\text{CaO}^*$  and  $\text{CaSO}_4^\dagger$  absorptions by hydrated oxides of iron and aluminium*

COMBINATION NUMBER	SOLIDS SUSPENDED IN 400 CC. AQUEOUS SOLUTION OF $\text{CaSO}_4^\ddagger$	MILLI-MOLS OF EITHER $\text{Fe}_2\text{O}_3$ OR $\text{Al}_2\text{O}_3$	CaO MILLI-MOLS PER MILLI-MOLS OF		CaSO <sub>4</sub> MILLI-MOLS PER MILLI-MOL OF		CaO-CaSO <sub>4</sub> ABSORPTION RATIO EXERTED BY	
			$\text{Fe}_2\text{O}_3$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{Al}_2\text{O}_3$
1	Oxide alone.....	2	....	....	0.02	0.06	....	....
2	Oxide alone.....	4	....	....	0.10	0.13	....	....
3	Oxide alone.....	8	....	....	0.12	0.11	....	....
4	Oxide and CaO.....	2	§	§	1.63	2.57	1.8	1.2
5	Oxide and CaO.....	4	2.75	3.10	1.21	1.48	2.3	2.1
6	Oxide and CaO.....	8	1.98	1.96	0.62	0.74	3.4	2.6
7	Oxide and quartz <sup>†</sup> .....	2	....	....	0.14	0.05	....	....
8	Oxide and quartz.....	4	....	....	0.07	0.10	....	....
9	Oxide and quartz.....	8	....	....	0.12	0.11	....	....
10	Oxide, CaO and quartz <sup>†</sup> ....	2	§	§	1.88	2.79	1.6	1.1
11	Oxide, CaO and quartz.....	4	3.05	3.07	1.16	1.47	2.4	2.1
12	Oxide, CaO and quartz.....	8	1.73	1.74	0.70	0.75	2.4	2.3

\* 1.0 gm. equivalent to 17.8 milli-mols.

† 125 gm.

‡ 0.8127 gm. equivalent to 5.97 milli-mols.

§ Solid phase  $\text{Ca(OH)}_2$  present.

part of the added lime that the titration values were considerably below saturation. From a comparison of the titration values of tables 3 and 4 it is evident that the lime-alumina reaction was more speedy than that between lime and  $\text{Fe}_2\text{O}_3$ .

The compilations of table 5 were made to bring out any quantitative relationships to be deduced from the absorption data of tables 3 and 4, and they indicate the formation of definite chemical compounds, with CaO,  $\text{Fe}_2\text{O}_3$  and  $\text{CaSO}_4$  as components in one case, and CaO,  $\text{Al}_2\text{O}_3$  and  $\text{CaSO}_4$  as components in the other case. It also appears that the total  $\text{CaSO}_4$  absorption is dependent not only upon the amount of reactive ferric or aluminic oxide,



but also upon the supply of  $\text{Ca}(\text{OH})_2$ . In spite of the insufficiency of  $\text{CaSO}_4$  in the  $\text{Al}_2\text{O}_3$  series, some evidence may be adduced by the molar-equivalence calculations.

It is evident that the maximal absorption of  $\text{CaO}$  per unit of  $\text{Al}_2\text{O}_3$ , or  $\text{Fe}_2\text{O}_3$ , was obtained in combinations 5 and 11. These combinations give the maximal titrations from the unabsorbed  $\text{Ca}(\text{OH})_2$  (tables 3 and 4) in the absence of solid phase hydrate. The maximal molar-proportion absorption of  $\text{CaO}$  by  $\text{Al}_2\text{O}_3$ , or  $\text{Fe}_2\text{O}_3$ , during a limited period of contact should come from the combination which maintained the largest amount of  $\text{Ca}(\text{OH})_2$  in the solution-phase. This maximum would be anticipated from combinations 4 and 10; but both of these still contained  $\text{Ca}(\text{OH})_2$  in the solid-phase. Combinations 5 and 11 gave the alkalinity titrations next in order. The residual  $\text{Ca}(\text{OH})_2$  in this pair of 4-milli-mol combinations was not equivalent to that necessary for a saturated solution, while the alkalinity values of the 8-milli-mol  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  combinations 6 and 12 fell still lower. In the case of the more reactive  $\text{Al}_2\text{O}_3$ , this third titration value proved to be a constant for the 48-hour and 16-day periods. The constant titration value of 1.1 cc. (table 4) evidently represents equilibrium under the imposed conditions.

From the average of the four  $\text{CaO}$  absorptions by  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  in combinations 5 and 11 (table 5) it appears that the molecular ratio between  $\text{CaO}$  and each of the two oxides is 1:3, when the  $\text{CaO}$  absorption is at its maximum. Furthermore, it appears that the  $\text{CaO}$  absorbed in combinations 6 and 12 was 35 per cent less than that in combinations 5 and 11. This may be explained on the ground that the lime charge afforded a  $\text{Ca}(\text{OH})_2$  concentration insufficient to force the reaction with 8 milli-mols beyond the points determined.

It has been pointed out that the maximum  $\text{CaSO}_4$  absorption per unit of  $\text{Fe}_2\text{O}_3$ , or  $\text{Al}_2\text{O}_3$ , could not be attained because of a deficiency in  $\text{CaSO}_4$ , especially for the larger charges of the two hydrated oxides. However, the maximum ratio would be expected from the minimum hydrated oxide charge. Combinations 4 and 10 of table 5 gave this result for both oxides. In the case of the more rapidly reacting  $\text{Al}_2\text{O}_3$ , the ratio of  $\text{Al}_2\text{O}_3$  to  $\text{CaSO}_4$  approaches 1 to 3, in combinations 4 and 10. But, because of the presence of solid-phase  $\text{Ca}(\text{OH})_2$  in combinations 4 and 10, it is necessary to use the  $\text{CaO-Al}_2\text{O}_3$  ratios indicated by combinations 5 and 11 in making deductions as to molar combinations. Since the absorbed  $\text{CaSO}_4$  and  $\text{CaO}$  are in the ratio of 1:1 when at maximum, then the ratio of both  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  to  $\text{CaSO}_4$  becomes 1:3, giving the rational formula of  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot n\text{H}_2\text{O}$  and its analogue  $3\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ .

Since these data are not sufficiently conclusive, however, for the definite determination of molecular proportions of  $\text{CaO}$  and  $\text{CaSO}_4$  to  $\text{Al}_2\text{O}_3$ , or  $\text{Fe}_2\text{O}_3$ , in the above mentioned absorption end-products, they are supplemented by those secured through further experimentation.

EXPERIMENT 3. THE NATURE OF THE  $\text{CaO}$  AND  $\text{CaSO}_4$  ABSORPTION PHENOMENA  
EXERTED BY ALUMINA GEL AND THE COMPOSITION OF END-PRODUCTS

The ferric and aluminic hydrated oxides behaved in a similar manner, but as the latter reacted more rapidly, it was used in the more comprehensive combinations of experiment 3. The gel used in the third experiment differed from that used in experiment 2. It was made by ammoniacal precipitation of an  $\text{HCl}$  solution of aluminium, instead of by the  $\text{NaOH}$  solution method used in obtaining the first hydrated product. The ammoniacal alumina precipitate was suspended in a large volume of water and filtered on a Büchner funnel. This process was repeated 5 times until peptization was noticeable. The flocculate was then dried in a water oven for 24 hours, yielding the gel used—a horny, translucent, yellowish-gray, granular material. Lumps of this material decrepitated and shattered into small glassy particles when immersed in water and remained in that condition indefinitely. In aqueous suspensions the granular gel had a very decided absorptive power for cochineal, which when absorbed from a golden yellow solution became crimson red within the gel. Its moisture content was 61.1 per cent, moisture-free basis. It was ground to pass a 100-mesh sieve. Charges of 0.3293 gm., the equivalent of 2 milli-mols of  $\text{Al}_2\text{O}_3$ , were weighed into the several flasks.

The lime used in experiment 3 was the same as that used in experiments 1 and 2. The calcium sulfate stock solution used was of such strength that each 50 cc. contained a 0.1324-gm.  $\text{BaSO}_4$  equivalent.

*CaO- $\text{Al}_2\text{O}_3$  series.* Two series of 500-cc. flasks were set up. One series was devoted to a study of the absorption of  $\text{CaO}$  by  $\text{Al}_2\text{O}_3$ , while the second was devoted to the absorption of both  $\text{CaO}$  and  $\text{CaSO}_4$ . Instead of the two charges of  $\text{CaO}$  used in experiment 1 and a 1-gm. constant as in experiment 2, lime was used in widely varying amounts. The minimum charge of  $\text{CaO}$  was equivalent to 2 milli-mols, with progressive increases of 2 milli-mols up to 20 milli-mols which gave ten 400-cc. combinations representing  $\text{Al}_2\text{O}_3$ - $\text{CaO}$  ratios from 1:1 up to 1:10.

At the end of the 24-hour, 48-hour and 96-hour periods of contact, 50-cc. aliquots were titrated against 0.5*N*  $\text{HCl}$ . Definite end-point titrations could not be obtained after reaction in the cold, because a part of the calcium aluminate was in a colloidal state. By boiling for a 1-hour period on a hot plate, with precautions against absorption of  $\text{CO}_2$ , it was found that this difficulty could be obviated and that the reaction was evidently expedited. After boiling, the colloidal calcium alluminate was deposited upon the sides of the flask as a hard, strongly adhering, white incrustation.

The data of table 6 demonstrate that equilibrium was obtained in each  $\text{CaO}$ - $\text{Al}_2\text{O}_3$  reaction within the 24-hour period. The slight variations in titration values for the 48-hour and 96-hour periods are well within experimental error. The closely agreeing aliquot titrations from combinations 2, 3 and 4 indicate that the readily hydrolized product, calcium aluminate,

gives a saturated 50-cc. aliquot requiring approximately 1.05 cc. of half normal acid. In combination 1 the maximum possible titration from the CaO addition would be equivalent to 1.05 cc. of half normal acid. As will be shown later, this amount of lime could combine with only one-third of the alumina present. In those combinations where the alkalinity was below that of one-half saturation of  $\text{Ca}(\text{OH})_2$  the solution was found to contain  $\text{Al}_2\text{O}_3$ . All combinations gave clear supernatants, but those of 5 to 10 showed very sharp end-points and no traces of  $\text{Al}_2\text{O}_3$ , proving that their titrations were derived solely from  $\text{Ca}(\text{OH})_2$ .

The titrations of table 6 were calculated to molecular proportions of CaO and  $\text{Al}_2\text{O}_3$  in the calcium-aluminate precipitates. After correction for the solubility of the lime-alumina precipitate, the results for combinations 1 to 7,

TABLE 6

*Periodic record of  $\text{Ca}(\text{OH})_2$  concentration in 400 cc. aqueous solution and total CaO absorption by suspensions of  $\text{Al}_2\text{O}_3$  gel and varying amounts of CaO\**

MILLI-MOLS OF CaO, PER MILLI- MOL OF $\text{Al}_2\text{O}_3$	TITRATION OF 50 CC. ALIQUOTS AGAINST 0.5 N ACID			FINAL CaO DISTRIBUTION			
	After 24 hours	After 48 hours	After 96 hours	Charge	Remaining in solution	Absorbed by 2 milli-mols of alumina gel	
	cc.	cc.	cc.	gm.	gm.	gm.	m.-mols
1	0.65	0.65	0.65	0.112	0.073	0.039	0.70
2	1.15	1.05	1.05	0.224	0.119	0.105	1.91
3	1.05	1.05	1.05	0.336	0.118	0.218	3.90
4	1.20	1.15	1.15	0.448	0.129	0.319	5.70
5	2.00	2.00	1.90	0.560	0.215	0.345	6.16
6	2.80	2.80	2.90	0.672	0.322	0.350	6.25
7	3.60	3.90	3.90	0.784	0.430	0.354	6.32
8	3.90	3.95	4.10	0.896	†	†	†
9	4.10	4.10	4.10	1.008	†	†	†
10	4.10	4.10	4.10	1.120	†	†	†

\* Compare with curve II, figure 1.

†  $\text{Ca}(\text{OH})_2$  in the solid phase.

appear as in table 7 and as curve III of figure 1. In the last four columns of table 6 the amounts of initial, unreacted, and absorbed lime are given in terms of gm. and milli-mols for the combinations devoid of solid-phase hydrate. From the last column of table 6 it is apparent that the CaO per milli-mol of gel increased up to combination 5 and that between combinations 5, 6 and 7 there was a near-constant increase. Two inherent errors which are applied to obtain the data of the last column in table 7 are involved at this point. The column headed "remaining in solution," table 6, is intended to represent the amount of  $\text{Ca}(\text{OH})_2$  which had not entered into combination with  $\text{Al}_2\text{O}_3$ . As given, however, the uncorrected data do not represent these values, since part of the titration values obtained were due to the solubility of calcium aluminate. This correction is, therefore, a variable, depending upon concen-

tration of  $\text{Ca}(\text{OH})_2$ , and it is dominant only within the narrow ratios of  $\text{CaO}$  to  $\text{Al}_2\text{O}_3$ . The second plus error, or minus correction, is applied in the two columns under the heading "in charge" (table 7). Though operative throughout the entire range of combinations, up to and including combination 7, it becomes a near-constant plus error in the range of ratios 5, 6 and 7 and amounts to approximately 4 per cent of the total  $\text{CaO}$  added to each combination. The data under the caption "Final  $\text{CaO}$  distribution," table 6, and the data of table 7 are graphed in figure 1 for the purpose of treating the entire series as a unit.

Curve 1 graphs absorption against final  $\text{CaO}$  concentrations, as determined by titration. Curve 2 represents absorption plotted against initial  $\text{CaO}$  additions, the absorption being based upon uncorrected titration values. Curve 3 represents values obtained after applying the 4 per cent plus error, or minus correction, on the basis of  $\text{CaO}$  charges and the similar solubility

TABLE 7

*Data from table 6 corrected for the solubility of a hypothetical calcium aluminate and a 4 per cent minus correction for  $\text{CaO}$  charges\**

MILLI-MOLS OF $\text{CaO}$ PER MILLI- MOL OF $\text{Al}_2\text{O}_3$	$\text{CaO}$		$\text{CaO}$	ABSORBED BY 2 MILLI-MOLS OF ALUMINA GEL	
	In charge		In solution		
	m. mols.	gm.	gm.	gm.	m.-mols
1	1.92	0.108	0	0.108	1.9
2	3.84	0.215	0	0.215	3.8
3	5.76	0.323	0	0.323	5.8
4	7.68	0.430	0.105	0.325	5.8
5	9.60	0.538	0.215	0.323	5.8
6	11.52	0.642	0.322	0.320	5.8
7	13.44	0.753	0.430	0.323	5.8

\* Compare with curve III, figure 1.

correction for the hypothetical calcium aluminate. It is apparent that the  $\text{CaO}$  absorptions were exactly equivalent to the amount of  $\text{CaO}$  added up to the value of 5.8 milli-mols, beyond which there was no increase, regardless of increase in the amount of lime charges. It thus appears that the end-product is represented by the proportion  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ , a compound having a solubility of 0.01  $N$  at  $25^\circ \text{C}$ .

Curve 1 should conform to the Freundlich adsorption isotherm, (1, 3, 13) if the changes in  $\text{Ca}(\text{OH})_2$  values were due to the physical, or surface, phenomenon. The dissimilarity between this curve and the Freundlich adsorption isotherm is such as to prove that the removal of  $\text{Ca}(\text{OH})_2$  from solution was not due to physical forces.

The indirect data as to the formation of the definite compound  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$  were supplemented by analyses of two precipitates. The first white crystalline material analyzed was obtained by boiling 5 milli-mols of powdered alumina gel for 1 hour in a liter of saturated solution of  $\text{Ca}(\text{OH})_2$ .

protected from the atmosphere during boiling and cooling. The precipitate was quickly filtered on a Büchner funnel and washed three times with distilled water and the crystals allowed to dry spontaneously. This material showed a strong adhesive tendency, forming a tenacious coating upon the glass containers. The second product was obtained by permitting the same proportions

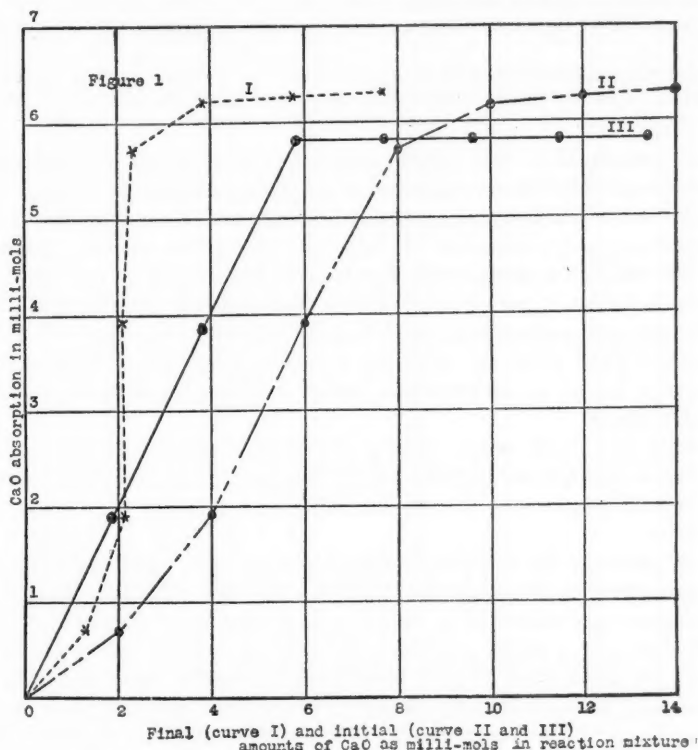


FIG. 1. ABSORPTION OF  $\text{CaO}$  BY ALUMINA GEL, AS AFFECTED BY VARYING AMOUNTS OF  $\text{Ca}(\text{OH})_2$

- I. Absorptions in equilibria with final concentrations.
- II. Absorptions plotted against amounts of  $\text{Ca}(\text{OH})_2$  added.
- III. Absorptions plotted against amounts of  $\text{Ca}(\text{OH})_2$  added. As corrected for solubility of calcium-aluminate and a constant experimental error of  $\pm 4$  per cent.

to remain at room temperature for 2 weeks with occasional agitation, glass beads being introduced to prevent cementation and nuclei inclusion. Without glass beads particles of  $\text{Al}_2\text{O}_3$  were included as nuclei and surrounded by periphery of the  $\text{CaO-Al}_2\text{O}_3$  reaction product, and later by the final product which included  $\text{CaSO}_4$  as a component.

The following results were obtained on aliquots from dilute HCl solutions of the two products:

	CaO	Al <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Laboratory product from <i>hot</i> solution.....	40.6	29.8	29.6
Theoretical for 3 CaO·Al <sub>2</sub> O <sub>3</sub> ·6H <sub>2</sub> O.....	44.4	27.0	28.6
Laboratory product after 2 weeks in <i>cold</i> .....	37.3	22.4	40.3
Theoretical for 3CaO·Al <sub>2</sub> O <sub>3</sub> ·10H <sub>2</sub> O.....	37.3	22.7	40.0

The formula 3CaO·Al<sub>2</sub>O<sub>3</sub>·6H<sub>2</sub>O approximates most closely the determined percentage of the three components in the product obtained by boiling. The excess of Al<sub>2</sub>O<sub>3</sub> and the consequential deficiency of CaO are in harmony with observations as to inclusions of Al<sub>2</sub>O<sub>3</sub> in the crystalline calcium aluminate.

The white precipitate obtained in the cold was very finely crystalline and upon agitation a portion of it readily dispersed into colloidal state. Its analyses gave results almost identical with those of the theoretical salt 3CaO·Al<sub>2</sub>O<sub>3</sub>·10H<sub>2</sub>O. From the foregoing, it appears quite possible that hydrates may be formed as intermediates between 3CaO·Al<sub>2</sub>O<sub>3</sub>·6H<sub>2</sub>O and 3CaO·Al<sub>2</sub>O<sub>3</sub>·10H<sub>2</sub>O.

*CaO-Al<sub>2</sub>O<sub>3</sub>-CaSO<sub>4</sub> series.* Having determined the fact that the reaction between Al<sub>2</sub>O<sub>3</sub> gel and Ca(OH)<sub>2</sub> solutions resulted in two hydrates of definite molecular proportions, the supplementary absorption of CaSO<sub>4</sub> was then studied.

In this series the 2-milli-mol constant of Al<sub>2</sub>O<sub>3</sub> with 2-milli-mol minimum, and of 20-milli-mol maximum, of CaO were also used. The lime and alumina additions were suspended in 400-cc. aqueous solutions of CaSO<sub>4</sub>, each 50 cc. of which gave a BaSO<sub>4</sub> precipitate of 0.1324 gm. At the end of 24, 48, 96, and 144 hours 50-cc. aliquots were drawn for titration and sulfate determinations. The data from the aliquot determinations and calculations showed that maximal absorptions of CaO had occurred, after the expiration of 96 hours, only in the first four combinations. In 5-milli-mol and 6-milli-mol combinations still further absorption had occurred between the 96-hour and 144-hour intervals; but the saturated combinations 7 to 10 contained solid-phase Ca(OH)<sub>2</sub>. However, practically complete CaSO<sub>4</sub> absorption took place, in all of the combinations from 3 to 10. It was therefore necessary to repeat the experiment with a larger volume of water, in order to insure an excess of CaSO<sub>4</sub>. In order to obviate the vitiating factor of varying temperature of the aqueous Ca(OH)<sub>2</sub>-CaSO<sub>4</sub> solution and to assure a constant initial value, the CaSO<sub>4</sub> content was maintained at a point below saturation. It was not, of course, known at the beginning of the experiment just how much calcium sulfate would be brought into reaction by the several CaO to Al<sub>2</sub>O<sub>3</sub> proportions.



In addition to caring for calcium sulfate deficiencies by increased volume, certain modifications were made to insure more exact computations and to minimize experimental error. In the first series, which contained insufficient  $\text{CaSO}_4$ , since it was also demonstrated that lime in excess of 6 milli-mols was

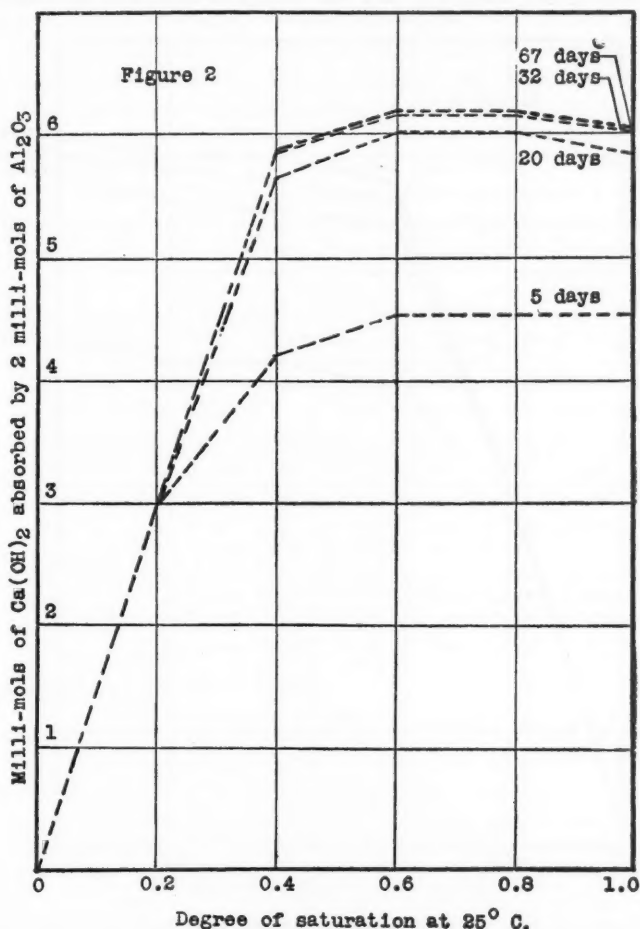


FIG. 2. SPEED OF  $\text{Ca}(\text{OH})_2$  ABSORPTIONS BY ALUMINA GEL, AS AFFECTED BY INITIAL  $\text{Ca}(\text{OH})_2$  CONCENTRATION

unnecessary, ratios up to 6 were used instead of the 10 used in the preliminary work. Maintaining the 2-milli-mol constant of  $\text{Al}_2\text{O}_3$ , and providing variables of  $\text{Ca}(\text{OH})_2$  concentrations, the analytical data of table 8 and the computations of table 9 were obtained. The results are also shown graphically in figures 2 and 3.

A large volume of a saturated solution of  $\text{Ca}(\text{OH})_2$  was made from the pure  $\text{CaO}$ . After attainment of equilibrium at laboratory temperature, the saturated solution was diluted with  $\text{CO}_2$ -free distilled water, so as to obtain 1 liter of each of the concentrations, 0.2, 0.4, 0.6, and 0.8 saturation. Freshly precipitated  $\text{CaSO}_4$  was added to a liter volume of these four concentrations

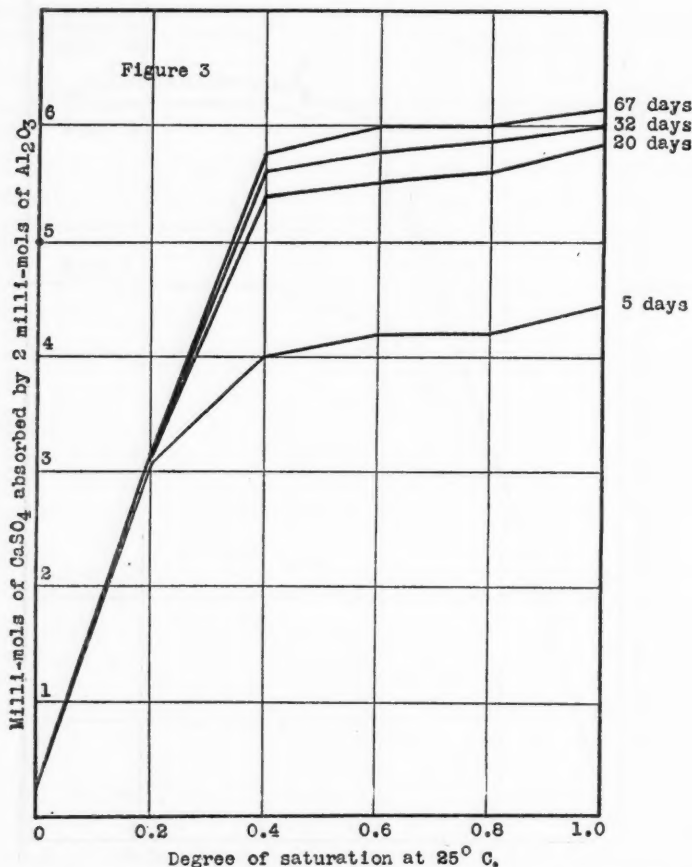


FIG. 3. SPEED OF  $\text{CaSO}_4$  ABSORPTIONS BY ALUMINA GEL, AS AFFECTED BY INITIAL  $\text{Ca}(\text{OH})_2$  CONCENTRATION

and also to the saturated  $\text{Ca}(\text{OH})_2$  solution. The solutions were shaken frequently during a 1-day period. The suspensions were then filtered, with precautions, and 750 cc. of each clear filtrate was used. Immediately upon introduction of these filtered solutions into the reaction flasks, aliquots of 50 cc. were drawn for  $\text{Ca}(\text{OH})_2$  titrations and  $\text{CaSO}_4$  determinations before the

introduction of the 2-milli-mol constant of powdered alumina gel. The flasks were then permitted to stand, with six daily agitations, until the conclusion of the final period of 67 days. Speed of the reaction, as influenced by the different concentrations of  $\text{Ca}(\text{OH})_2$  and the near-constant concentration of  $\text{CaSO}_4$  was obtained by aliquot withdrawals at the end of 5 days, 20 days, 32 days and 67 days. The initial volume of 700 cc. had been decreased, therefore, to 500 cc. at the conclusion of the final contact period. The changes in concentrations were consequently not exactly proportional to the total absorptions. Computations were made for each period by applying the factor necessitated by reduction in volume at each period.

From table 8 it is evident that equilibrium was obtained in combination 2 at the end of the 5-day period. Equilibria in the combinations 3 to 6 were obtained at the end of the 20-day period. The milli-mol values for combinations 4, 5 and 6 (table 9) for the 20-day, 32-day and 67-day periods are

TABLE 8

*Periodic aliquot determinations of  $\text{Ca}(\text{OH})_2$  and  $\text{CaSO}_4$  in aqueous solution after contact with 2 milli-mols of alumina gel—750 cc. initial volume; varying concentrations of  $\text{Ca}(\text{OH})_2$  and near-constant initial concentration of  $\text{CaSO}_4$*

COMBINATION NUMBER	TITRATION OF 50 CC. ALIQUOT AGAINST 0.5 N ACID					$\text{BaSO}_4$ EQUIVALENT OF $\text{CaSO}_4$ IN 50-CC. ALIQUOTS				
	Initial*	After 5 days	After 20 days	After 32 days	After 47 days	Initial*	After 5 days	After 20 days	After 32 days	After 47 days
	cc.	cc.	cc.	cc.	cc.	gm.	gm.	gm.	gm.	gm.
1	0	0	0	0	0	0.1926	0.1865	0.1860	0.1865	0.1865
2	0.90	0.05	0.05	0.05	0.05	0.1590	0.1072	0.1060	0.1057	0.1062
3	1.90	0.70	0.25	0.25	0.20	0.1510	0.0842	0.0595	0.0554	0.0517
4	2.60	1.30	0.85	0.85	0.80	0.1478	0.0774	0.0540	0.0490	0.0442
5	3.40	2.10	1.65	1.65	1.60	0.1370	0.0668	0.0415	0.0384	0.0358
6	4.10	2.80	2.40	2.40	2.30	0.1440	0.0700	0.0455	0.0422	0.0386

\* Before introduction of powdered  $\text{Al}_2\text{O}_3$  gel.

remarkably close to the values of  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4$ . It will be remembered that, when converted to totals, any analytical errors were increased by the factors 11, 12, 13 and 14. Averaging the three  $\text{Ca}(\text{OH})_2$  titration values from combinations 4, 5 and 6 for the last three periods and averaging the residual sulfate values for corresponding combinations and periods we have the formulas,  $3.06\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2.89\text{CaSO}_4$ ,  $3.06\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2.92\text{CaSO}_4$  and  $2.98\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2.99\text{CaSO}_4$ . The differences between the sulfate residuals are not great for the periods of 20, 32 and 47 days; but in each case there is a steady approach toward the theoretical of 3 milli-mols. It is, therefore, conclusively shown that the absorption of  $\text{Ca}(\text{OH})_2$  and  $\text{CaSO}_4$  by hydrated  $\text{Al}_2\text{O}_3$  is due to the formation of a definite chemical compound, rather than to adsorption. From these data, as also from preceding data, it is also evident that the  $\text{CaSO}_4$  reaction with the calcium aluminate lags somewhat behind the reaction between calcium hydroxide and alumina. Similar

TABLE 9  
Speed of the  $\text{Ca}(\text{OH})_2$  and  $\text{CaSO}_4$  reactions with 2 milli-mols of  $\text{Al}_2\text{O}_3$  gel suspended in 700 cc. aqueous solution of  $\text{Ca}(\text{OH})_2$ - $\text{CaSO}_4$  at different contact periods, as affected by varying initial concentrations of  $\text{Ca}(\text{OH})_2$

COMBINATION NUMBER	INITIAL CONCENTRATIONS OF $\text{Ca}(\text{OH})_2$		$\text{CaO}$ REMOVED FROM SOLUTION AFTER												$\text{CaSO}_4$ REMOVED FROM SOLUTION AFTER																			
	Saturation factor*	Normality value	5 days				20 days				32 days				47 days				5 days				20 days				32 days				67 days			
			gm.	mm. mols	gm.	mm. mols	gm.	mm. mols	gm.	mm. mols	gm.	mm. mols	gm.	mm. mols	gm.	mm. mols	gm.	mm. mols	gm.	mm. mols	gm.	mm. mols	gm.	mm. mols	gm.	mm. mols	gm.	mm. mols						
1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.0440	0.32	0.0440	0.32	0.0440	0.32	0.0440	0.32	0.0440	0.32	0.0440	0.32					
2	0.2	0.009	0.1673	2.99	0.1673	2.99	0.1673	2.99	0.1673	2.99	0.1673	2.99	0.1673	2.99	0.1673	2.99	0.1673	2.99	0.4229	3.10	0.4229	3.10	0.4320	3.17	0.4341	3.19	0.4309	3.16	0.4309	3.16				
3	0.4	0.019	0.2352	4.20	0.3171	5.67	0.3255	5.81	0.3263	5.83	0.3263	5.83	0.3263	5.83	0.3263	5.83	0.3263	5.83	0.5454	4.00	0.5454	4.00	0.7327	5.38	0.7614	5.59	0.7851	5.76	0.7851	5.76				
4	0.6	0.026	0.2548	4.55	0.3367	6.01	0.3367	6.01	0.3451	6.16	0.3451	6.16	0.3451	6.16	0.3451	6.16	0.3451	6.16	0.5748	4.22	0.5748	4.22	0.7522	5.52	0.7872	5.78	0.8180	6.00	0.8180	6.00				
5	0.8	0.034	0.2548	4.55	0.3367	6.01	0.3367	6.01	0.3451	6.16	0.3451	6.16	0.3451	6.16	0.3451	6.16	0.3451	6.16	0.5743	4.22	0.5743	4.22	0.7661	5.62	0.7995	5.87	0.8162	5.99	0.8162	5.99				
6	1.0	0.041	0.2548	4.55	0.3276	5.85	0.3276	5.85	0.3360	6.00	0.3360	6.00	0.3376	6.03	0.3376	6.03	0.3376	6.03	0.6042	4.44	0.6042	4.44	0.7899	5.80	0.8130	5.97	0.8361	6.14	0.8361	6.14				

\* Approximations at working temperature, averaging 25°C.

CaO-CaSO<sub>4</sub> absorptions were also obtained by the use of several aluminium minerals as well as soils.

The parallel between the Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> reactions with Ca(OH)<sub>2</sub> and CaSO<sub>4</sub> is well defined, with variation in speed and completeness, and it is evident that the reaction between Ca(OH)<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub> and CaSO<sub>4</sub> is likewise a purely chemical phenomenon.

#### CHEMICAL DETERMINATIONS ON THE ISOLATED CRYSTALLINE CaO-Al<sub>2</sub>O<sub>3</sub>-CaSO<sub>4</sub> END-PRODUCT

The white crystalline precipitate obtained from combination 4 of table 9 had the molecular proportions of 3.09 CaO and 3.00 CaSO<sub>4</sub> to one of Al<sub>2</sub>O<sub>3</sub>, as represented by the difference between the 0.026 *N* solution of Ca(OH)<sub>2</sub> saturated with CaSO<sub>4</sub> initially and the final Ca(OH)<sub>2</sub> and CaSO<sub>4</sub> concentrations after 47 days contact with 2 milli-mols of Al<sub>2</sub>O<sub>3</sub>. This precipitate was air-dried and analyzed for CaO, Al<sub>2</sub>O<sub>3</sub>, CaSO<sub>4</sub> and water of crystallization. A 2-gm. charge was dissolved in HCl and made to a volume of 250 cc. Twenty-five cubic centimeter aliquots were used for duplicate CaO determinations, 25 cc. for SO<sub>3</sub> and 75 cc. for Al<sub>2</sub>O<sub>3</sub>. Loss on ignition was obtained by heating two charges of 0.4275 gm. The results are given in table 10.

TABLE 10

*Analysis of calcium-alumino-sulfate absorption compound as compared with theoretical composition and that of a volcanic occurrence reported by Dana (2)*

MATERIAL	DETERMINED COMPONENTS				
	CaO	Al <sub>2</sub> O <sub>3</sub>	SO <sub>2</sub>	H <sub>2</sub> O	Total
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Theoretical salt.....	26.40	8.00	18.90	46.70	100.00
Volcanic product.....	27.27	7.76	16.64	45.82	97.49
CaO-Al <sub>2</sub> O <sub>3</sub> -SO <sub>4</sub> absorption product.....	27.60	8.33	18.40	46.20	100.53

The agreement with theory is very close and complete confirmation of the indirect-method data is established.

#### PREVIOUS RELATED OBSERVATIONS

No reference has been found as to the occurrence of the calcium-alumino-sulfate and calcium-ferro-sulfate described and illustrated in this contribution, insofar as their formation in soils is concerned. Only scant reference to calcium aluminate was found, while calcium ferrate has not been mentioned.

The supposed aluminic compound 3CaO·Al<sub>2</sub>O<sub>3</sub> is assumed by Mirasol (11, p. 175) to account for the elimination of aluminium after soil treatments of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and KNO<sub>3</sub>, where Al<sub>2</sub>(NO<sub>3</sub>)<sub>6</sub> results from extractions with the potassium salt. Equations were balanced, using CaCO<sub>3</sub> [limestone rather than Ca(OH)<sub>2</sub>]; but no experimental evidence was given as to the formation of the calcium aluminate. Reasoning from the occurrence of calcium alu-

minate in Portland cement, Mirasol (11, p. 186) twice refers to the salt as a "very stable compound." No experimental evidence was given in substantiation of this statement. As made in the present contact studies, simulating soil conditions, we have found the calcium aluminates,  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$  and  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$  to be appreciably soluble in water, readily subject to decomposition by  $\text{H}_2\text{CO}_3$  and readily reactive with  $\text{CaSO}_4$ , forming the salt  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 33\text{H}_2\text{O}$ .

From the soil viewpoint Vincent (12) studied the reaction between suspensions of ferric and aluminic hydrated oxides and  $\text{Ca}(\text{OH})_2$ . He found an insoluble, white crystalline precipitate of calcium aluminate, to which he gave the formula  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ . He likewise found complete precipitation of iron upon addition of  $\text{Ca}(\text{OH})_2$ , the precipitate containing  $\text{Fe}_2\text{O}_3$  and  $\text{CaO}$  in amounts approaching unimolecular proportions.

The only available reference to a natural occurrence of calcium-alumino-sulfate, with substantiative analytical data, is that of Dana (2), who gives the analysis of Ettringite by Lehmann (4), table 10, as  $6\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 33\text{H}_2\text{O}$ . This formula was derived from the analysis of a 0.36-gm. charge cavity occurrence in a limestone inclusion in lava. The lava specimen was given as colorless, transparent, needle-like, prismatic crystals, seldom more than 3 mm. in length and 0.1 to 0.5 mm. thick.

#### MICROSCOPIC EXAMINATION OF CALCIUM COMBINATIONS WITH ALUMINIUM AND IRON, WITH AND WITHOUT THE SULFATE RADICAL

The photomicrographs of the several ferric and aluminic compounds under high power are given in plate 1. All crystals examined were colorless. It will be remembered that two calcium-alumino hydrates were obtained.

*Calcium aluminates*— $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ . When examined between crossed Nicols these crystals, obtained on boiling, remained dark upon complete rotation of the microscopic stage. Since this observation was true for all crystals in view, in spite of any attempt to change their orientation, it may be concluded that the crystals belong to the isometric system. However, it should be remembered that crystals of either the tetragonal, or hexagonal, systems standing on their C axes would behave in a similar manner. Convergent polarized light was not available and the crystal system could not, therefore, be determined by an examination for interference figures. The system is believed to be further established by the following detailed microscopic observations of structure:

The crystals are very thick and give broad contour bands in water medium. A projection view of the crystals gave a 6-sided outline. Upon careful focusing with high-power lens, 4 bounding edges of a rhombic plane were in evidence. With slight downward focusing 2 more appeared to extend outward from the obtuse angles. These 2 edges, together with the 4 in the horizontal plane, appeared as intersections of 4 rhombic planes at an angle with the horizontal. This conforms to the orientation of a dodecahedron lying upon any one of its faces 1:100. The constancy of this view, together with the optical isotropy of the calcium aluminate crystals, indicates the isometric, or cubic system of the dodecahedron form.



The crystals— $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$ —obtained after extended contact at room temperature were considerably smaller than those obtained by boiling. They were very thin plates of hexagonal outline and resembled closely those of calcium ferrate. Examined between crossed Nicols with C axis parallel to optic axis, they remained dark. In other positions the crystals appear as elongated twisted shapes, which show parallel extinction and produce polarization colors with maximum intensity at  $45^\circ$ .

*Calcium-alumino-sulfate.* These crystals were formed from several different aluminic compounds and in each case there was obtained the spherulite formation with acicular individuals on the periphery. Except when agitated with glass beads, the nucleus of the spherulite was generally found to be a particle of the original alumina gel, or the intermediate product calcium aluminate, formed by the reaction of  $\text{Ca}(\text{OH})_2$  upon the gel. The largest crystals were obtained when the alumina suspension in  $\text{Ca}(\text{OH})_2$ - $\text{CaSO}_4$  solution was allowed to stand undisturbed for from 2 to 3 days at room temperature without agitation or more than an occasional gentle rotation.

Examination of the individual crystals with polarized light and between crossed Nicols showed parallel extinction. This indicates the hexagonal crystallization system and agrees with Lehmann's observations on the mineral specimen, as quoted by Dana (2).

It will be noted that the calcium-alumino-sulfate was obtained not only from alumina gel, but also from a Rhode Island soil, secured through the kindness of Dr. P. S. Burgess.

*Calcium ferrate.* No difficulty was experienced in the preparation of the calcium-ferrate crystals. However, the reaction between the dried hydrated ferric oxide powder and lime water did not proceed to the completeness found in the case of alumina. Because of this fact, it was not feasible to separate the crystals from the unreacted  $\text{Fe}_2\text{O}_3$ , consequently no direct chemical analysis could be made. Calcium ferrate crystals were obtained also after 10 days' contact between moist precipitate  $\text{Fe}_2\text{O}_3$  and a saturated solution of  $\text{Ca}(\text{OH})_2$ . Very fine crystals were also obtained by mixing a ferric chloride solution with a large excess of  $\text{Ca}(\text{OH})_2$ . This latter procedure gave a product of a gelatinous nature, and though some crystals were present, they were exceedingly minute and occluded in the agglutinated masses of hydrated  $\text{Fe}_2\text{O}_3$ . These crystals are most probably those mentioned by Mellor (10), who states: "Thus calcium ferrate  $\text{Ca}(\text{FeO}_2)_2$ , that is,  $\text{CaO} \cdot \text{Fe}_2\text{O}_3$  is made by precipitating a neutral solution of ferric chloride with lime water."

The appearance and dimensions of the tri-calcium ferrate crystals may be seen from the photomicrographs. The crystals were found to be extremely thin and apparently of relatively low refractive index as judged by the narrow contour bands in water media. They were so extremely brittle and so readily fractured by agitation only a few perfect forms may be observed in the mass of imperfect crystals. The perfect crystals appear as regular hexagonal plates, whose angles measure  $120^\circ$ . With polarized light and between crossed

Nicols, the thin crystals remained dark on complete rotation of the stage. This optical isotropy conforms to the behavior of any hexagonal crystal in section normal to its C axis, as appears to be the natural position of the crystals examined.

A very characteristic shimmering effect is produced by the rotation of suspensions containing the  $3\text{CaO} \cdot \text{Fe}_2\text{O}_3$  crystals and a residuum of the ferric oxide gel in  $\text{Ca}(\text{OH})_2$  solutions. This wave effect was not observed, however, when the ferric chloride solutions were treated with an excess of  $\text{Ca}(\text{OH})_2$ .

*Calcium-ferro-sulfate crystals.* The same difficulty of incomplete reaction and presence of hydrated ferric oxide, noted in the case of the calcium ferrate crystals, was experienced when the combinations of calcium hydroxide, ferric hydroxide and  $\text{CaSO}_4$  were permitted to stand. The white crystals,  $3\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 9\text{H}_2\text{O}$  resemble, in a general way, those of the calcium-alumino-sulfate; but they are considerably shorter and of greater thickness. Differing from its aluminum analogue, calcium-ferro-sulfate appears as crystals in pairs or groups of three crossing each other and it does not give the spherulite formation. These crystals also show parallel extinction hence it is most probable that they belong to the hexagonal system.

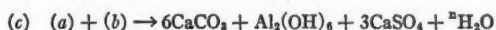
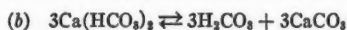
#### SOLUBILITY OF THE CALCIUM-ALUMINO-SULFATE

By reference to reports upon previous lysimeter leachings (6, 7, 8) it will be noted that persistence of causticity and depressed sulfate outgo were parallel. With the present findings at hand, the question arises whether the resumption of sulfate leachings was due in part to solution of the sulfate precipitate, or its hydrolysis after disappearance of  $\text{Ca}(\text{OH})_2$ , or solely to activated sulfonation induced by the accumulation of  $\text{CaCO}_3$ . The previous laboratory studies (9) showed that sulfates retained by soil suspensions in the presence of  $\text{Ca}(\text{OH})_2$ , were readily extracted after conversion of hydroxide to carbonate. The calcium-alumino-sulfate, formed by additions of  $\text{Ca}(\text{OH})_2$  and  $\text{CaSO}_4$  to the alumina gel, was found to be insoluble in strong solutions of either  $\text{Ca}(\text{OH})_2$  or  $\text{CaSO}_4$ .

The solubility of pure calcium-alumino-sulfate in  $\text{CO}_2$ -free distilled water was determined after intermittent agitation for 3 days, and 2 weeks additional contact. The clear extract was analyzed for alkalinity, total  $\text{CaO}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SO}_3$ . In terms of milli-mols, these respective values were found to be 1.00, 2.02, 0.31 and 1.14. The proportions represented by these data show that the calcium-alumino-sulfate undergoes little, if any, hydrolysis in pure water and that it has a 0.00033 molar solubility. The theoretical requirement of  $\text{Al}_2\text{O}_3$  per liter for solution without hydrolysis is 0.0340 gm., while the amount found was 0.0317 gm.

But in the lysimeters the excesses of  $\text{Ca}(\text{OH})_2$  were converted to  $\text{CaCO}_3$ , which leached as bicarbonate along with sulfates. Simulating these conditions, 22.5-gm. charges of calcium-alumino-sulfate were introduced into two

400-cc. volumes of  $\text{CaH}_2(\text{CO}_3)_2$  in equilibrium at  $25^\circ \text{C}$ ., with titration values of 3.75 cc. and 1.35 cc. of 0.5 *N* acid per 100 cc. After 16 hours both solutions gave a 0.5 *N* titration of 0.3 cc. The strong solution gave a  $\text{BaSO}_4$  determination of 0.2100 gm. per 100 cc. as against 0.0925 gm. for the weaker solution. These data show a decomposition of calcium bicarbonate with proportionate liberation of  $\text{CaSO}_4$  from the calcium-alumino-sulfate, as represented by 0.94 milli-mols and 0.90 milli-mols per 100 cc. for the decomposed carbonate and liberated sulfate, respectively, in the stronger solution, while similar milli-mol values of 0.34 and 0.40 were found for the weaker solution aliquot. The reactions may be expressed by the equations:



It is, therefore, apparent that the absorbed salt releases sulfate readily to leachings from soil containing  $\text{CaCO}_3$ . Since  $\text{Al}_2\text{O}_3$  was absent from solution—differing from the  $\text{CO}_2$ -free aqueous extract—it is further evident that the sulfate-releases in this experiment were due to the disintegration of the calcium-alumino-sulfate. The same is most probably true as to the less readily formed calcium-ferro-sulfate, which could not be obtained free from unreacted hydrated  $\text{Fe}_2\text{O}_3$ .

From related laboratory experiments it is known that sulfonation was inhibited by the heavy lime additions during the persistence of causticity. The small outgo of sulfates from the heavily limed tanks may be attributed then to; (a) suspended sulfonation, (b) fixation of soil sulfates by the formation of calcium-alumino-sulfate and calcium-ferro-sulfate, and (c) the partial fixation of the sulfates of rainfall through formation of the same two salts. It may be assumed also that initially, at least, the resumption of sulfate leachings from the lysimeters was due in large measure to the disintegration of the two alumino and ferro salts. But, in time, after the disappearance of the excess of  $\text{Ca}(\text{OH})_2$ , through leaching and carbonation, renewed and activated sulfonation may have been responsible for a part of the sulfate outgo.

*Significance.* The findings solve the problem as to repressed outgo of sulfates observed in examination of the leachings from the heavily limed loam. It also shows that  $\text{Ca}(\text{OH})_2$  may not be used indiscriminately in flocculating soil suspensions, if soluble sulfates are to be determined. Additional information is also derived as explaining the reason for a part of the absorption of  $\text{CaO}$  by soils in aqueous suspensions.

The formation of the calcium-alumino-sulfate and its subsequent disintegration may have a very practical relation in agriculture, as explaining the disintegration of concrete tile when embedded in soil. Infusion of sulfate-impregnated waters into the mass of concrete would result in changing calcium-

aluminate hydrates, adhesion and cohesion materials, into calcium-alumino-sulfate, a crystalline non-adhesive substance. This material is appreciably soluble in soft water and it is decomposed by carbonated water. Both processes would materially change the physical structure and tensile strength of the concrete. With the resultant increase in porosity, disintegration would be accelerated. The difference in densities is shown by the settling volumes of 2-milli-mol constants of  $\text{Al}_2\text{O}_3$ , as the gel  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ ,  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$  and  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 33\text{H}_2\text{O}$  (plate 1). The practical application of the findings as applied to cements and plasters, will be treated elsewhere.

#### SUMMARY

A study was made of the factors whereby heavy additions of burnt lime inhibited the outgo of native sulfates, rainfall sulfates, and sulfates derived from additions of  $\text{FeSO}_4$ , pyrite, and powdered sulfur in lysimeter leachings, and of those responsible for extensive and immediate absorptions of sulfates in soil-lime, ignited-soil-lime and commercial lime suspensions.

Silica,  $\text{Fe}_2\text{O}_3$ , and  $\text{Al}_2\text{O}_3$ , the predominant components of soil and ignited-soil, were used singly and in combination with  $\text{Ca}(\text{OH})_2$  as absorbing solids in aqueous suspensions, in lieu of the indefinite soil complex.

Solid-phase  $\text{Ca}(\text{OH})_2$ , derived from pure  $\text{CaO}$ , did not exert the same absorption previously found with commercial lime (experiment 1).

Ground quartz and precipitated silicic acid suspensions showed negligible absorption with or without lime. Precipitated silicic acid was quickly converted to the inactive silicate. Ferric oxide alone showed slight absorption, but  $\text{Fe}_2\text{O}_3$ - $\text{Ca}(\text{OH})_2$  combination absorbed large quantities of sulfates (experiment 1).

$\text{Ca}(\text{OH})_2$  and  $\text{CaSO}_4$  constants and variables of freshly precipitated  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  gave titrations and sulfate determinations which showed absorptions of both  $\text{CaO}$  and  $\text{CaSO}_4$  in amounts indicative of molecular proportions. Definite analogy between absorptive properties of  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  was established in the proportions  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4$  and  $3\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot 3\text{CaSO}_4$ , with greater speed characterizing the alumina reactivities (experiment 2).

With  $\text{Ca}(\text{OH})_2$  as a variable and  $\text{CaSO}_4$  and  $\text{Al}_2\text{O}_3$  as constants, a parallel study of  $\text{CaO}$ - $\text{CaSO}_4$  absorption was made; solubilities of absorption products were given and the results as to the influence of concentration and time were graphed (experiment 2).

Sulfate absorption was found to depend upon and follow the  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  and  $3\text{CaO} \cdot \text{Fe}_2\text{O}_3$  reactions, the speed of the  $\text{CaSO}_4$  absorption by  $3\text{CaO} \cdot \text{Fe}_2\text{O}_3$  being less rapid than that of  $\text{CaSO}_4$  combination with  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  (experiment 2).

From titrations,  $\text{CaO}$  was found to combine with  $\text{Al}_2\text{O}_3$  in definite proportions of 3- $\text{CaO}$  to 1- $\text{Al}_2\text{O}_3$ , while the analysis of the end-products showed the two hydrates,  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$  and  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$  as resulting

from hot and cold reactions, respectively,  $(3\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O})$  was formed only in the cold) (experiment 3).

Using constant volumes, varying concentration of  $\text{Ca}(\text{OH})_2$ , near-constant initial concentration of  $\text{CaSO}_4$  and a molar constant of  $\text{Al}_2\text{O}_3$ , equilibrium was attained and positive confirmation of molar equivalences was secured (experiment 3).

End-products obtained in experiment 3 were subjected to chemical analyses which established the composition of the alumina absorption end-product as  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 33\text{H}_2\text{O}$ ; but, because of the presence of unreacted  $\text{Fe}_2\text{O}_3$  in the ferric oxide analog, the composition  $3\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot n\text{H}_2\text{O}$  is necessarily assigned thereto.

Solubilities and dissociation of the several materials were determined in water and in aqueous solution of  $\text{Ca}(\text{OH})_2$ , and also of  $\text{CaSO}_4$ .

The disintegration of pure  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 33\text{H}_2\text{O}$  by action of  $\text{CaH}_2(\text{CO}_3)_2$  in equilibrium is shown by analyses and accounted for by equations.

The crystallography of the several materials,  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ ,  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$ ,  $3\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ ,  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 33\text{H}_2\text{O}$  and  $3\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot n\text{H}_2\text{O}$  is given.

The determination of the progressive  $\text{CaO}$  absorption by  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ , absolute absorption and retention of sulfate during persistence of  $\text{Ca}(\text{OH})_2$  and the decomposition of  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 33\text{H}_2\text{O}$  in  $\text{CaH}_2(\text{CO}_3)_2$  solution, giving  $\text{Al}_2\text{O}_3$  deposition and  $\text{CaSO}_4$  liberation, served to explain sulfate fixation and subsequent liberation in heavily limed soil in lysimeter experiments and laboratory suspensions.

Photomicrographs are given of the crystals of  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  compounds, previously undescribed and unisolated in soil chemistry literature, together with graphs of the speed of reaction and photographs showing settling volumes of  $\text{CaO} \cdot \text{Al}_2\text{O}_3$  and  $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4$  salts from aqueous suspensions.

The studies demonstrate the fallacy of the indiscriminate use of lime as a coagulant in the determination of soluble sulfates and possibly other compounds. They may be considered as indicative of and as typifying other absorptions, since definite chemical reactions have been established accounting for what otherwise might be considered as typical adsorption phenomena.

Practical application of the findings are suggested, as accounting for the disintegration of soil-embedded concrete.

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## PLATE 1

- FIG. 1. Calcium aluminate,  $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 10\text{H}_2\text{O}$ .  
 FIG. 2. Calcium aluminate,  $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$ .  
 FIG. 3. Calcium aluminate,  $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$ .  
 FIG. 4. Calcium-alumino-sulfate,  $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 33\text{H}_2\text{O}$  (from gel).  
 FIG. 5. Calcium-alumino-sulfate,  $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 33\text{H}_2\text{O}$  (from gel).  
 FIG. 6. Calcium-alumino-sulfate,  $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 33\text{H}_2\text{O}$  (from soil).  
 FIG. 7. Calcium ferrate,  $3\text{CaO}\cdot\text{Fe}_2\text{O}_3\cdot ^n\text{H}_2\text{O}$ .  
 FIG. 8. Calcium ferrate,  $3\text{CaO}\cdot\text{Fe}_2\text{O}_3\cdot ^n\text{H}_2\text{O}$ .  
 FIG. 9. Calcium-ferro-sulfate,  $3\text{CaO}\cdot\text{Fe}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot ^n\text{H}_2\text{O}$ .





FIG. 1.  $\times 300$

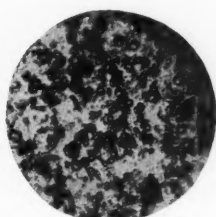


FIG. 2.  $\times 50$



FIG. 3.  $\times 300$

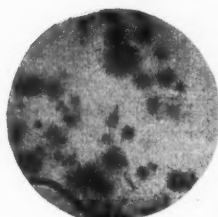


FIG. 4.  $\times 50$



FIG. 5.  $\times 300$



FIG. 6.  $\times 300$

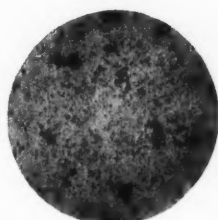


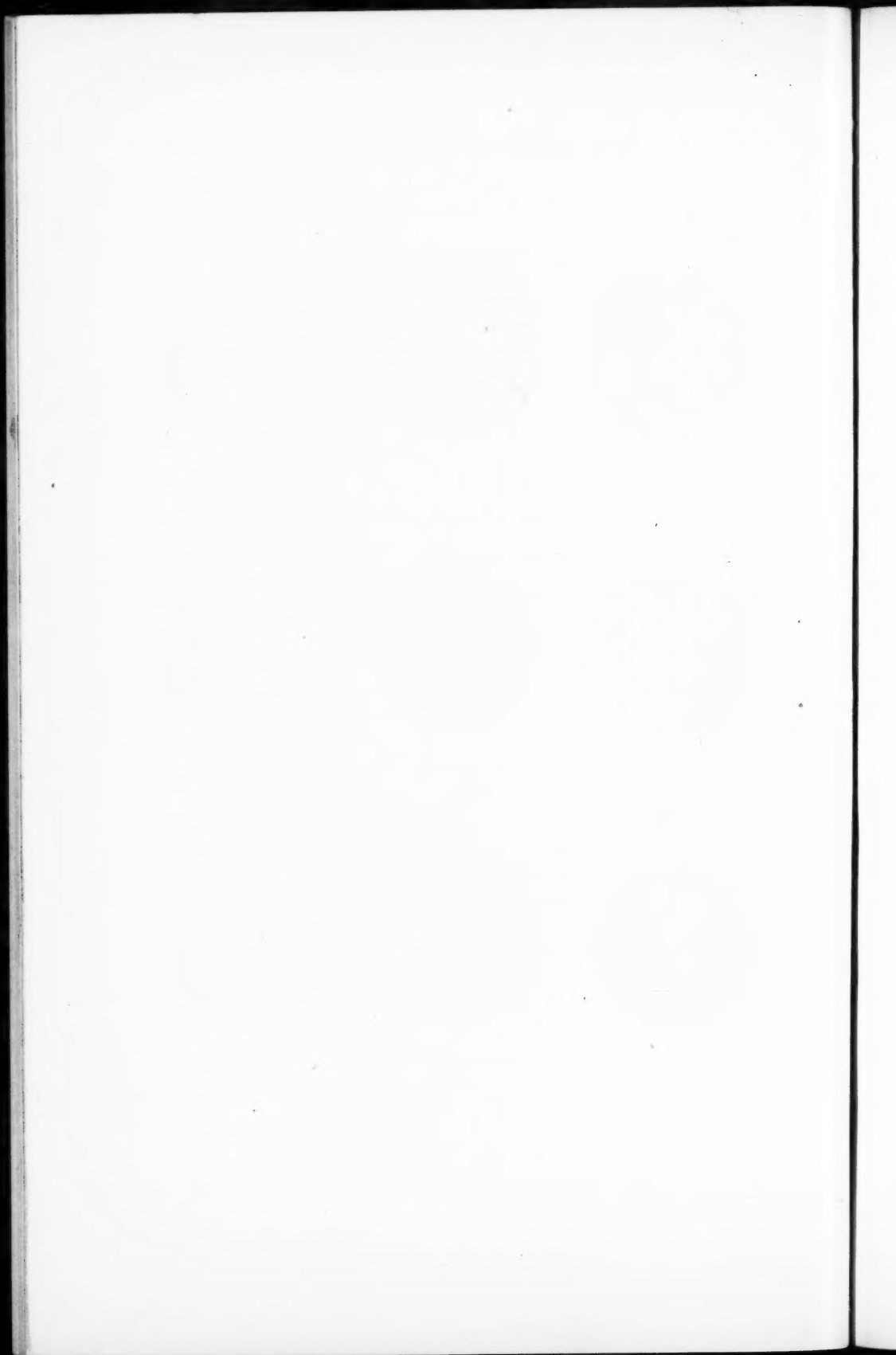
FIG. 7.  $\times 50$



FIG. 8.  $\times 300$



FIG. 9.  $\times 300$



## THE HEAT OF WETTING AS A NEW MEANS OF ESTIMATING THE COLLOIDAL MATERIAL IN SOILS

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One of the greatest needs in soil studies is a method for determining the amount of colloidal material in soils, for it now appears quite certain that the amount is much greater than has been believed heretofore and that most of the chemical and physical properties and reactivities of soils are due mainly to their colloids. Such phenomena as adsorption of chemical reagents, moisture adsorption and retentiveness, heat of wetting, unfree water, rate of evaporation of water, plasticity and cohesiveness are all closely associated with or mainly controlled by the colloids in the soil. To understand and compare intelligently the different soils with one another it is essential, therefore, to know their colloidal content.

### PREVIOUS METHODS

Various methods have been proposed from time to time for estimating the colloidal content of soils. The most important are the methods of Schloesing (10), Hilgard (7), Williams (13), Sokol (11), Scales and Marsh (9), Ashley (1), Mitcherlich (8), Tempany (12) and the United States Bureau of Soils (6).

The methods of Schloesing, Hilgard, Williams, Sokol, and Scales and Marsh are based upon the general principle of isolation for estimating the colloids in the soil. These investigators assumed that most or all of the colloidal material could be brought into suspension by agitating the soil with water. In view of our present knowledge, however, this assumption is quite erroneous, for it is not an easy matter to execute the isolation of colloids from the soil with water. The experience at this laboratory shows that it takes long-continued rubbing and agitation with a very large number of washings before much of the colloids can be extracted from the soil, and in many cases, only a very small amount can be isolated. The above methods, therefore, cannot give a true and complete estimation of the colloidal content.

Ashley's and Mitcherlich's methods are based upon the principle of adsorption for the colloidal-content estimation, the former with the use of malachite green dye, the latter with water vapor. In both methods the whole soil was used for the adsorption and no attempt was made to isolate the colloids, consequently these methods can give only a relative estimation of the colloidal

content. Furthermore, Ashley's method may not even indicate the true relative colloidal content because the dye has a high specific adsorbability; and since different soils have more or less different kinds of colloids, the dye will be absorbed differently. This latter objection may apply also to water vapor, but as will be shown subsequently, water is more of a universal reagent and its adsorption by the different colloids may not differ so greatly as that of the dye.

Tempany's method for the estimation of the colloidal content is based on the shrinkage of the soil upon drying. It does not seem that this method can give a true estimation of the colloidal content, as different kinds of colloids have different expansion coefficients especially when a comparison is made between the organic and inorganic colloids. Furthermore, it appears that the method cannot be very accurate.

The United States Bureau of Soils method is based upon the same principle as that of Mitcherlich, namely, the adsorption of water vapor; but this method makes the important advance of determining the adsorption of water vapor, not only of the whole soil but also of the colloids extracted from that soil. By knowing the adsorptive capacity of the whole soil and of its colloids, the amount of colloids present can be quantitatively estimated by the ratio:

$$\frac{\text{adsorption per gram of soil}}{\text{adsorption per gram of colloid}} \times 100$$

It seems very probable that of all the various methods described above, that of the Bureau of Soils, comes closest to giving a true estimation of the colloidal content of soils.

#### THE HEAT OF WETTING AS A NEW METHOD

For some time the writer has been interested in trying to work out a method for determining the colloidal material in soils. As early as 1920 he believed that in the property of heat of wetting there might be found a method for this determination, as the work he was then doing on the heat of wetting of soils (2) clearly indicated that the fine, or colloidal material was mainly responsible for this phenomenon. In a seminar of that year he suggested the use of the heat of wetting as a method for determining the colloids in the soil. The further work that has been done at this laboratory upon the subject, has confirmed his idea. That the property of heat of wetting is due mainly if not entirely to colloidal material is indicated by the fact that non-colloidal material even in a very fine state of division, does not produce heat of wetting. For instance, rocks and minerals ground to an extremely fine condition fail to give any measurable amount of heat of wetting. Even soil colloids which give a tremendous amount of heat of wetting in their natural state fail to give any after being ignited, even though ground so fine as to stay in suspension indefinitely. Again, when the colloids are extracted from a soil, its heat of wetting is greatly reduced.

It is the object of this paper, therefore, to present the heat of wetting as a new means of estimating the colloidal material in soils. The method has already been proposed in a preliminary note (5), and this paper contains a more detailed account of the method and data.

It appears that this method has many advantages over the other methods, including the Bureau of Soils method, as it is much simpler, far more rapid, and should be more accurate. In the vapor-adsorption method many days are required for equilibrium to be established, while the heat of wetting method requires only a few minutes. In the adsorption method, certain errors may enter, such as condensation due to changes in temperature and uncertainty as to when equilibrium is reached, which do not apply to the heat of wetting method.

#### *Procedure*

The procedure consists of determining the heat of wetting of the soil, then extracting a certain amount of colloids from the soil and determining their heat of wetting. Knowing the heat of wetting of both the whole soil and its extracted colloids, the colloidal content can be readily calculated by the ratio:

$$\frac{\text{heat of wetting in calories per gram of soil}}{\text{heat of wetting in calories per gram of colloid}} \times 100$$

The heat of wetting of both the soil and the colloid was determined according to the method described in a former publication (3). It consists of placing about 50 gm. of air-dry soil and about 15 gm. of colloid or any small amount that was available, in a wide glass tube and allowing it to dry in an electrically heated oven at a temperature of about 107° for about 24 hours. The tube was then taken out, closed quickly and tightly with a rubber stopper and allowed to attain the room temperature. After the exact weight and temperature were ascertained, the soil or colloid was quickly and carefully poured into a calorimeter containing 100 gm. of water, and the heat of wetting was ascertained. Extreme care was taken before mixing to have both the soil and water at exactly the same temperature and very nearly that of the room temperature. In order not to impart any heat to the soil material while it was being poured into the calorimeter, the tube containing it was held between very thick flannel cloth. In order to be able to convert, if necessary, the rise of temperature into heat calories, the water equivalent of the calorimeter was determined. This was found to be 25 gm. of water. For specific heat the value of 0.200 was used for mineral soil, and 0.300 for organic soils.

The colloids were extracted from the soil by suspending about 500 gm. of soil in about 1 liter of water. The mixture was allowed to stand for 24 hours and the supernatant liquid siphoned off. The sediment was then poured into a large pan and rubbed thoroughly with the hand, to hasten and facilitate extraction and dispersion of the colloids. The sediment was then washed back into the beaker and diluted to the original volume. After the mixture stood

for another 24 hours, the previous procedure was repeated, and followed by similar treatment at least five times, involving the use of about five liters of water for each soil extraction.

The supernatant or siphoned liquid was then centrifuged at a speed of about 1500 revolutions per minute for 20 minutes and the material that remained in suspension after this centrifuging was regarded as consisting mostly of colloids. The liquid was evaporated<sup>1</sup> at a temperature of about 55°C. and the heat of wetting of this colloidal material was determined as described above.

The sediment that settled at the bottom of the tubes during centrifuging was collected, and after evaporation, its heat of wetting was also determined. This was done in order to ascertain what differences if any, existed between it and the material that remained in suspension after centrifuging.

#### EXPERIMENTAL RESULTS

##### *Colloidal content*

The results on the heat of wetting of both the whole soil and its extracted colloids, together with calculated colloidal content as obtained by the ratio:

$$\frac{\text{heat of wetting in calories per gram of soil}}{\text{heat of wetting in calories per gram of colloid}} \times 100$$

are shown in table 1 for 8 different types of soil, namely, Rhode Island sandy loam, Pennsylvania silt loam, Michigan silt loam, Michigan silt loam, Minnesota Carrington clay loam, California adobe clay, Michigan clay, (U. P.) and Michigan clay (Saginaw).

TABLE 1  
*Colloidal content of soils*

NAME OF SOIL	HEAT OF WETTING PER GRAM OF SOIL	HEAT OF WETTING PER GRAM OF COLLOID	PERCENTAGE OF COLLOID INDICATED
	<i>calories</i>	<i>calories</i>	<i>per cent</i>
1. Rhode Island sandy loam.....	2.877	16.280	17.67
2. Pennsylvania silt loam.....	1.850	8.226	22.50
3. Michigan silt loam.....	7.100	12.380	57.35
4. Michigan silt loam.....	6.545	10.060	65.12
5. Minn. Carrington clay loam.....	9.340	10.550	56.44
6. California adobe clay.....	8.280	16.190	51.12
7. Michigan clay (U. P.).....	6.396	9.070	70.56
8. Michigan clay (Saginaw).....	8.688	12.750	68.18

The results reveal at once the most striking fact that the colloidal content of soils as determined by the heat of wetting method is comparatively very high, the amount ranging from 17.67 per cent in the Rhode Island sandy loam to 70.56 per cent in Michigan clay (U. P.). The soils used in this investigation are average representative types and it cannot be said that they are unusual in their colloidal content. This extraordinary and unexpected high colloidal content, therefore, is contrary to the general belief, which had its origin with

<sup>1</sup> The colloids, of course, can be concentrated more quickly by means of the supercentrifuge.



Schloesing, that soils contained only from 0.5 to 1.5 per cent of colloidal material. On the other hand, these results agree with those of the Bureau of Soils (6) who found that in 32 different types of soils investigated the amount of colloidal material ranged from 6 to 70 per cent. The results of both investigations, therefore, strongly tend to confirm the fact that the colloidal content of soils is much higher than has been believed heretofore.

*Comparison between material in suspension and that settled in centrifuging*

The colloidal content of soils as given above is based upon the material which stayed in suspension after 24 hours and also after centrifuging the supernatant liquid for 20 minutes at a speed of about 1500 revolutions per minute as stated previously. After centrifuging the supernatant liquid, some of the suspended material was thrown out, and settled at the bottom of the tube. The question arose, is this fine material that settles in centrifuging different from that which

TABLE 2  
*Comparison in the heat of wetting between material stayed suspended and that settled in centrifuging*

NAME OF SOIL	HEAT OF WETTING PER GRAMS OF SUSPENDED MATERIAL	
	Suspended material	Settled material
	calories	calories
1. Rhode Island sandy loam.....	16.280	15.430
2. Pennsylvania silt loam.....	8.226	5.949
3. Michigan silt loam.....	12.380	11.600
4. Michigan silt loam.....	10.060	9.800
5. Minn. Carrington clay loam.....	16.550	18.440
6. California adobe clay.....	16.190	15.280
7. Michigan clay (U. P.).....	9.070	8.260
8. Michigan clay (Saginaw).....	12.750	10.500

remains in suspension? There appeared two possibilities, (a) that the suspended material may be different both chemically and physically from that which settled and (b) that the settled material may be practically the same both chemically and physically as that which remained in suspension, but its colloidal particles still remained in the undispersed condition and settled out. To throw light upon these questions, therefore, the heat of wetting of the settled material also was determined. The results obtained are shown in table 2, together with the results of the suspended material for comparison.

Table 2 shows that there are only slight differences in the heat of wetting between the suspended colloids and the material which settled. These results would tend to suggest, therefore, that probably all the material of a soil which stays in suspension for 24 hours, is similar and may be classed as colloidal.

It also appears that the colloidal material which is extracted from a soil in the first four or five extractions is identical, and is a fair representative of the

colloidal material that remained in the soil unextracted. This is strongly suggested by the fact that the amount of colloidal material found in a soil by the heat of wetting method agrees fairly closely with the amount of colloids extracted, plus the amount of colloids remaining in the extracted soil as indicated by the ratio:

$$\frac{\text{heat of wetting in calories per gram of extracted soil}}{\text{heat of wetting in calories per gram of colloid}} \times 100$$

Thus for instance, in the Michigan clay (U. P.) the quantity of colloids as calculated by the percentage indicated by the heat of wetting method was 355.75 gm. in 500 gm. of soil. The amount of material separated plus that remaining in the soil as indicated by the above ratio approximates the same amount. This agreement held in practically all the soils investigated.

#### *The variability of colloids in different soils*

While it appears that the colloidal material within a soil might be so uniform that a sample extracted may be a fairly good representative of the whole, at

TABLE 3  
*Difference in heat of wetting of colloids from different soils*

NAME OF SOIL	HEAT OF WETTING PER GRAM OF COLLOIDS
	<i>calories</i>
1. Rhode Island sandy loam.....	16.280
2. Pennsylvania silt loam.....	8.226
3. Michigan silt loam.....	12.380
4. Michigan silt loam.....	10.060
5. Minnesota Carrington clay loam.....	16.550
6. California adobe clay.....	16.192
7. Michigan clay (U. P.).....	9.070
8. Michigan clay (Saginaw).....	12.750

least in most soils, the colloids of different soils vary considerably, at least in their physical condition. Table 3 shows, for comparison, the heat of wetting in calories per gm. of colloids in the different soils.

An examination of these results at once reveals the fact that the heat of wetting of the colloids from the different soils varies considerably. In some soils the difference between the highest and lowest values is more than 50 per cent. This difference in the heat of wetting must denote, therefore, that the colloids in the various soils are different from each other. Since they are not the same and give different heat of wetting values, it does not seem possible that a factor could be used to estimate accurately the colloidal content of soils from their heat of wetting. This phase of the investigation is being further studied, but at present it seems that any factor established can be expected to give only an approximate estimation of the colloidal content of soils. On the other hand, in many soils in which it is almost impossible to disperse and

extract their colloids, the application of this factor would be very useful. To establish a reliable factor, however, a large number of soils must be investigated. This work is now being done.

THE POSSIBLE CAUSES FOR THE DIFFERENCE IN THE HEAT OF WETTING OF THE COLLOIDS FROM DIFFERENT SOILS

A chemical and physical consideration would seem to suggest that the colloids in the different soils may vary both chemically and physically and, thereby give different heat of wetting values. From the chemical standpoint the soil colloids consist mainly of organic matter and of hydrated iron-aluminum silicates. A chemical determination was made of all these constituents in the foregoing colloids and while no definite relationship was revealed between the percentage of these colloidal constituents and the heat of wetting, yet in determinations of heat of wetting of artificial aluminum hydroxide, ferric hydroxide and silica gel, all three of which were obtained from the Chemical Warfare Service, and also of peat and muck containing a very low ash content, showed the following heat of wetting values per gram of material: aluminum hydroxide, 20.87 calories; ferric hydroxide, 9.37 calories; silica gel, 24.00 calories; peat, 20.10 calories; muck, 34.42 calories. The heat of wetting of these materials varies considerably. It would seem reasonable to infer, therefore, that when these colloidal constituents are present in different proportions in the colloids of different soils, the heat of wetting will vary accordingly. It has also been noticed that when colloids have carbonates present, their heat of wetting is reduced. This is to be expected in view of the fact that carbonates do not produce heat of wetting.

Probably a most important cause for the difference of the colloids from different soils, lies in their physical condition. Much of the evidence accumulated would indicate that colloids from various soils possess surfaces of different degrees of activation which cause the colloids to react differently with water. Substances possessing no active surfaces will be almost inert, although they may be extremely fine. It would seem that the reactivity of material depends not entirely upon its fineness of division, but also upon the degree of activation, and that the reactivity may be more important than the size of its particles. That this idea of activated surface appears reasonable is supported by the fact that rocks and minerals ground extremely fine, show no reactivity with water, as they give no heat of wetting, although soils which were formed from such rocks and minerals, give large amounts of heat of wetting. Again when soil colloids which give tremendous amounts of heat of wetting are ignited they lose their activity and do not regain it, no matter how finely they are ground. In this connection it might be argued that when the colloids are ignited their total surface is tremendously reduced and cannot be brought back by grinding. That is true, but the total surface is not reduced to 100 per cent as is the activity or heat of wetting. The heat of wetting method tends to determine, therefore, not only the amount of colloidal material in soils but also its state of activation.

The next question is what causes this difference in activated surface or reactivity of materials. There appear to be several factors which may be responsible for the phenomenon. The most important of these are the degree of decomposition and the nature of surface, i.e., whether it is porous, smooth, or vitrified.

Because of the specific adsorbability of the different reagents by the various colloids, and because the various colloidal constituents exist in different soils in different proportions, and also on account of the different reactivity of the colloids in the different soils, the colloidal content of soils as determined by the various reagents cannot be comparable. However, since water is the most universal reagent it would seem that this is best to employ for the estimation of the colloidal content of soils.

#### STABILITY OF COLLOIDS

Although the physical condition of colloids from different soils appears to vary, the physical condition of colloids from the same soil seems to be quite stable and does not change easily. This is strongly indicated by the fact that on heating (4) soils at various temperatures from 100 to 800°C., it was found that their heat of wetting did not begin to be affected perceptibly until a temperature of about 200°C. was reached. Heating the colloids at these high temperatures for several hours is such a severe treatment that if they resist a change, they must be quite stable. Through long and continued changes in the weathering process, such as drying, wetting, and freezing, the soil colloids, especially those at the surface soil, must have reached equilibrium and thus have become stabilized. Hence the process of extracting the colloids from the soil and drying them at the temperature of 105°C. as is done in the heat of wetting method, probably does not in any way alter the colloids, and consequently no error is introduced in the results.

On the other hand, soil colloids that are still fresh, such as those found in deep horizons, both in inorganic and organic soils, may not be so stable, and they undergo some alterations when they are heated, but in this case, even air-drying will affect them, making them irreversible.

#### SUMMARY

The property of heat of wetting is presented as a new means of estimating the colloidal material in soils. The method consists of determining the heat of wetting of the soil, then extracting a certain amount of colloids from the soil and determining also their heat of wetting. With the heat of wetting of both the soil and extracted colloids known, the colloidal content can be readily calculated.

The method of heat of wetting is simple, very rapid and accurate, and appears to be superior to the vapor-adsorption and dye-adsorption methods.

The property of heat of wetting appears to be due almost entirely to the colloidal material, and very little, if any, to the non-colloidal material.

According to the heat of wetting method the amount of colloidal material present in soils is much higher than has heretofore been believed. The amount found in the soils investigated varies from 17.67 per cent in a sandy loam to 70.56 per cent in a clay, with most of the clays and clay loam containing more than 50 per cent.

One of the interesting things revealed by this method is the fact that reactivity of material may not depend entirely upon the size of its particles but also upon the state of activation. The latter may be due to several factors, such as degree of decomposition, nature of surface, i.e., whether it is porous, smooth or vitrified.

The colloidal material in soils appears to be quite stable and is not easily altered.<sup>2</sup>

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<sup>2</sup> Since this paper was prepared and sent to the publishers, there has appeared in the Journal of Agricultural Research, May 31, 1924, but issued in November, 1924, an article by M. S. Anderson entitled, "The Heat of Wetting of Soil Colloids," in which the heat of wetting is proposed as a method of estimating the colloidal material in soils. It is very interesting and significant that Anderson's results agree with those of the author and go to show that the heat of wetting presents an excellent means of determining the colloidal material in soils.

Anderson's paper was received by the Journal of Agricultural Research on July 2, 1924. The present writer, however, first suggested the method in February, 1924 (Soil Sci., v. 17, p. 135-139) and sent a note to Science on April 24, 1924, which was not published until Oct. 3, 1924 (Science, Oct. 3, 1924, v. 40, no. 1550, p. 230). Science, however, does not follow the practice of publishing the date at which the papers are received. On the other hand (in a paper read before the Second Annual Colloid Symposium, at Northwestern University, June, 1924) the writer definitely proposed the method of heat of wetting as a new means of estimating the colloidal material in soils. This paper together with others, is being published as a Colloid Symposium Monograph by the American Chemical Society.

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